ATOMIC WEIGHT OF THE PRINCIPAL ELEMENTS.

According to the Report of the International Commission for 1911.

Element	Symbol	Weight	Element	Symbol	Weight
Aluminium	Al	27.1	Magnesium	Mg	24.32
Antimony	Sb	120.2	Manganese	Mn	54.93
Arsenic	As	74.96	Mercury	Hg	200.0
Barium	Ba	137.37	Molybdenum	Mo	96.0
Beryllium	Be	9.1	Nickel	Ni	58.68
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Cæsium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.09	Platinum	Pt	195.2
Carbon	C	12.00	Potassium	K	39.10
Chlorine	Cl	35.46	Rhodium	Rh	102.9
Chromium	Cr	52.0	Rubidium	Rb	85.45
Cobalt	Co	58.97	Silicon	Si	28.3
Copper	Cu	63.57	Silver	Ag	107.88
Fluorine	F	19.0	Sodium	Na	23.00
Gold	Au	197.2	Strontium	Sr	87.63
Hydrogen	H	1.008	Sulphur	S	32.07
Iodine	I	126.92	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.85	Tungsten	W	184.0
Lead	Pb	207.10	Uranium	U	238.5
Lithium	Li	6.94	Zinc	Zn	65.37

QUALITATIVE ANALYSIS

TOWER

A COURSE OF

Qualitative Chemical Analysis

OF

Inorganic Substances,

WITH EXPLANATORY NOTES ... *2d ed.*

BY

OLIN FREEMAN TOWER, Ph. D.

HURLBUT PROFESSOR OF CHEMISTRY IN ADELBERT COLLEGE OF WESTERN
RESERVE UNIVERSITY

SECOND EDITION, REVISED

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1012 WALNUT STREET
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PREFACE TO THE SECOND EDITION.

The general style of the book has not been changed in this edition; but many of the directions for procedure have been rewritten, additional notes added, and some different methods of separation introduced. The nitroso-beta-naphthol method for the separation of cobalt and nickel is the one now given in the text, but the potassium-nitrite method is retained in the notes for the use of those who prefer it or who do not have the former reagent at hand. A shorter method is given in the notes for the precipitation of the Iron group, which some may prefer, as it obviates the tedious filtration of the basic acetates. The method of separating strontium and calcium by the use of amyl alcohol can only be employed in a laboratory provided with well-working hoods; consequently another method has been given in the notes which does not require the use of this reagent. The Solubility Table has been considerably enlarged.

The author desires to express his thanks to all those who have favored him with suggestions with regard to improvements in the book, and he will welcome any additional criticism which will help toward the same end.

<div align="right">O. F. T.</div>

Cleveland, January, 1911.

PREFACE TO THE FIRST EDITION.

Some apology is necessary for the appearance of another text-book of Qualitative Analysis. Most of the briefer treatises on this subject are entirely inadequate in the treatment of the subject from the modern standpoint and in the lack of precautionary directions which are necessary to secure delicacy of reaction in the hands of students. Some seem to think that they have partially compensated for this by introducing several pages of equations for reactions, many of which may or may not be in accord with the facts, and all of which tend to kill initiative on the part of the student. Then there is another class of text-books on this subject which leave nothing to be desired in the points just mentioned, but which are filled with a mass of descriptive matter, seldom consulted by the student and making the book bulky and expensive. This text seeks to avoid these difficulties. For all descriptive matter the student is referred to Edwin Lee's Experimental Chemistry and to Alexander Smith's General Chemistry for Colleges, which give all the material of this sort ever required in an elementary course of Qualitative Analysis. The presentation of the subject is modern, and explanatory notes are given, wherever required, and arranged in such a way on the page opposite the directions for procedure that they may be consulted without special effort on the part of the student.

A brief statement of the special principles derived from Physical Chemistry, which are of most frequent application in Qualitative Analysis, is given in the introduction. Although these principles may be found in the books just referred to, it was thought advisable to present them here in concise and connected form. The student who has become acquainted with them in his elementary work may be helped by finding them here in a form suitable for ready reference, while the student to whom they are strange must become acquainted with them, if he wishes to master anything more than the mechanical processes of the subject. But few

equations for reactions are given, in order to encourage the student to work them out for himself. All skeleton outlines of procedure have been omitted, for, according to the experience of the author, students are apt to follow them blindly, and thereby fail to secure delicacy of reaction, which can result only from careful manipulation accompanied by a knowledge of the full directions of procedure and of the explanatory notes.

Under the Acid Analysis it is emphasized that the tests are tests for the acid radicals, or anions, as students frequently gain the idea from many books from such headings as "Test for Hydrochloric Acid," etc., that they are testing for free acids. The tests are therefore given here under the name of the radical, and the accompanying symbol is that of the corresponding ion (see pp. 57–65). Although the method of treatment presupposes an elementary knowledge of the ionic hypothesis, the author has endeavored to avoid overemphasizing it. Ionic formulas are freely employed, but whenever a knowledge of the actual salts in solution is of more importance molecular formulas are given (see p. 26).

With few exceptions the methods of separation employed are the standard ones. For the separation of antimony from tin the method of Noyes and Bray is employed, which depends on the insolubility of antimony sulphide in hot 8 per cent. hydrochloric acid. This obviates the use of the troublesome hydrogen generator, and has, in the hands of students in this laboratory, given uniformly better results than the standard method. The basic acetate method is used for the precipitation of the Iron group. This gives an excellent separation if properly conducted. The instructor must give the student considerable personal attention the first few times it is tried, after which no special difficulties are experienced. An optional method for precipitating this group along with the Zinc group by means of ammonium hydroxide and ammonium sulphide is given in the appendix for the benefit of those who do not care to employ the basic acetate method. The sodium peroxide method is used for the separation of chromium. This method has now, however, come into such general use that no apology for its employment is necessary. Strontium is separated from calcium by the amyl alcohol method.

This has been in use in this laboratory for over ten years, and when employed in the manner described is rapid and yields very uniformly accurate results in the hands of students.

The general order of procedure followed by the author is indicated on pp. 15–18. The modifications introduced in the Iron and following groups by the presence of phosphates and oxalates is not taught to the student until he begins to prepare solutions himself from solid substances, for such cases cannot arise unless the original substance is insoluble in water. Some may prefer to teach students at the outset how to prepare solutions, pp. 70–76, in which case the method to be employed when phophates and oxlates are present should be included when the Iron group is first taken up.

The analysis of the Potassium group is carried out entirely by means of the flame and spectroscope tests. In the experience of the author, students have less success in using the precipitants commonly recommended for the metals of this group than with the simple tests mentioned.

The groups of the metals are named from one of the principal metals of each group rather than being designated by a number. Methods of numbering differ so much in different books, that the names used here seem to preclude all possibility of ambiguity that might arise from the employment of the other method. No index is given, as the table of contents is sufficiently detailed, so that everything ought to be found without difficulty.

It is hoped that this text will appeal to those teachers who wish a concise treatise along modern lines, which will encourage the student not only to carry out accurately the mechanical processes of Qualitative Analysis, but also to apply some of the principles of modern chemistry in his practical work.

O. F. T.

TABLE OF CONTENTS.

QUALITATIVE ANALYSIS.

INTRODUCTION.

It is taken for granted throughout this book that the student is acquainted with the principal features of the ionic hypothesis (L. C., Chap. 14; S. C., Chap. 19).[1] According to this hypothesis, all acids, bases, and salts in aqueous solution are more or less dissociated into ions; the metals, metallic groups (as NH_4), and hydrogen constituting the positive, or cations, and the non-metals and acid radicals constituting the negative ions, or anions.

Cations will always be designated by their symbols with one or more dots above, indicating the number of positive charges carried by each gram-ion; anions will be designated similarly, but with the negative charges indicated by accent marks, thus: $\overset{\cdot}{H}$, $\overset{\cdot}{NH_4}$, $\overset{\cdot}{Hg}$, $\overset{\cdot\cdot}{Hg}$, $\overset{\cdot\cdot\cdot}{Al}$, Cl', NO_3', SO_4'', PO_4''', etc. These are named as follows in the order just given; hydrogen ion, ammonium ion, mercurous ion, mercuric ion, aluminium ion, chloride ion, nitrate ion, sulphate ion, phosphate ion, etc.

Since in Qualitative Analysis one has to do primarily with substances in solution, one deals largely with reactions between ions. It is therefore of the greatest importance that the student be familiar with the nature of the more common electrolytes and the principles which govern their double decompositions. Electrolytes which are only slightly dissociated into ions, or as it is frequently termed ionized (less than 1% in normal solution), are called "weak"; those which are more than 20% ionized in normal solution are called "strong"; those whose degree of ionization lies between these limits are classed as "moderately strong." This classification applies especially to acids and bases. Most salts belong to the second class. The degree of dissociation, it should be remembered, increases as the concentration decreases. A

[1] Throughout this book L. C. refers to Edwin Lee's "Text-book of Experimental Chemistry" and S. C. to Alexander Smith's "General Chemistry for Colleges."

table of the degree of dissociation of many of the more common electrolytes is given in the Appendix, p. 79.

REVERSIBLE REACTIONS. The majority of chemical actions are incomplete; this is especially true of reactions in solution with which we have the most to do in Basic Analysis. These reactions are incomplete on account of the operation of two opposite tendencies, one carrying the reaction forward, the other between the products formed, tending to reproduce the original components and thus reverse the reaction. For example:

$$NaC_2H_3O_2 + HCl \rightleftarrows HC_2H_3O_2 + NaCl.$$
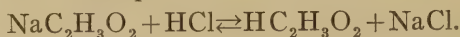
Sodium acetate and hydrochloric acid in solution react by double decomposition, yielding acetic acid and sodium chloride. But as soon as the latter are formed they begin to interact with each other and form sodium acetate and hydrochloric acid. Finally the reverse reaction proceeds with the same speed as the forward action and equilibrium results, all four substances being present. Equilibrium is, therefore, a state of poise or balance between the two opposing tendencies. Such reactions are consequently called balanced actions or reversible reactions.

The speed with which a reaction proceeds is governed by the specific tendency of the substances to combine (affinity) and by their concentrations. With regard to the latter we have the law: **The speed of a chemical reaction is proportional to the molar concentrations of the reacting substances.** In the above reaction, letting c_1, c_2, c_3, and c_4 be the concentrations at equilibrium of the four substances in the order in which they occur in the written equation, the forward reaction is then proceeding at the speed, $S = kc_1c_2$, and the reverse reaction at the speed, $S' = k'c_3c_4$. The letters k and k' represent constants (the temperature being constant), depending upon the specific tendency of the substances to combine. Since equilibrium has been reached

$S = S'$, and therefore $kc_1c_2 = k'c_3c_4$, or $\dfrac{c_3c_4}{c_1c_2} = \dfrac{k}{k'}$. But $\dfrac{k}{k'}$ is constant,

therefore,

$$\frac{c_3c_4}{c_1c_2} = K \qquad\qquad (1)$$

in which K is called the equilibrium constant.

It is seen at once from the nature of the equation, that if we increase c_1, the concentration of one of the original components, the reaction will go forward so as to increase c_3 and c_4, the concentrations of the resulting substances; else the constancy of the expression will not be preserved. Likewise, for the same reason, if c_3, the concentration of one of the resulting substances, is increased, the reaction will be reversed to increase c_1 and c_2. If, therefore, it is desired to carry the reaction further toward completion to the right, it may be done by greatly increasing the concentration of one of the original substances.

Decreasing the concentration of one of the resulting substances will, however, accomplish the same thing. We therefore strive, when we desire to bring an action to completion, to produce a substance which is either volatile or insoluble. In such a case the amount of the substance remaining in solution (which is all that can come into active contact with the molecules of the other substances) is very small, and hence the reaction goes forward nearly to completion. Two such reactions are:

$$NaCl + H_2SO_4 \rightleftarrows NaHSO_4 + HCl \uparrow,$$
$$BaCl_2 + Na_2SO_4 \rightleftarrows BaSO_4 \downarrow + 2NaCl.$$
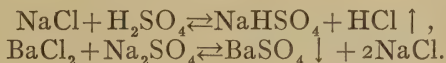
In the first one the arrow pointing upward shows that the HCl is volatile and escapes. In the other the arrow pointing downward indicates that $BaSO_4$ is insoluble. Since these reactions go practically to completion, we may omit the reverse arrow, and write them thus:

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow,$$
$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 \downarrow + 2NaCl.$$
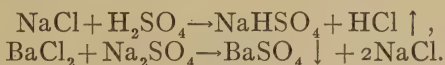
The dissociation of an electrolyte is a reversible reaction, and hence is governed by the same principles as any reversible action. The ionization of acetic acid may be represented thus:

$$\underset{c}{HC_2H_3O_2^1} \rightleftarrows \underset{c_1}{H^{\cdot}} + \underset{c_2}{C_2H_3O_2'},$$
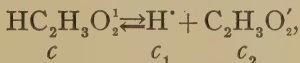
and at equilibrium we have as above,

$$\frac{c_1 c_2}{c} = K \tag{2}$$

[1] The heavy arrow pointing to the left indicates that at equilibrium the concentration of the undissociated substance exceeds that of the ions.

Reactions in solution are reactions between ions.

REACTIONS BETWEEN IONS. The complete formulation of the reaction between barium chloride and sodium sulphate, cited above, is,

$$BaCl_2 \rightleftarrows \overset{..}{Ba} + 2Cl'$$
$$Na_2SO_4 \rightleftarrows SO_4'' + 2\overset{.}{Na}$$
$$\Updownarrow \qquad \Updownarrow$$
$$(disslv'd) \ BaSO_4 \quad 2NaCl$$
$$\Updownarrow$$
$$(insol.) \ BaSO_4 \downarrow$$
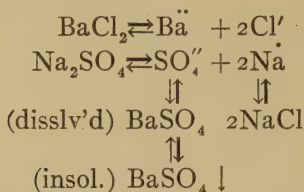
Some $\overset{..}{Ba}$ and SO_4'' ions unite, and since $BaSO_4$ is quite insoluble, as fast as some forms it precipitates, and all the reactions are displaced toward the right. NaCl being highly ionized, the $\overset{.}{Na}$ and Cl' ions remain in the solution, and but little un-ionized NaCl is formed. This is indicated by the heavier arrow pointing upward. The principal reaction can therefore be indicated thus:

$$\overset{..}{Ba} + SO_4'' \rightarrow BaSO_4 \downarrow .$$
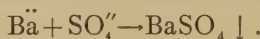
When two electrolytes are mixed, the reaction between them is commonly negligible unless an insoluble substance results as above, or unless one of the products is but slightly ionized. This latter case is illustrated by the neutralization of an acid by a base. When solutions of sodium hydroxide and nitric acid are employed, the formulation is as follows:

$$NaOH \rightleftarrows \overset{.}{Na} + OH'$$
$$HNO_3 \rightleftarrows NO_3' + \overset{.}{H}$$
$$\Updownarrow \qquad \Updownarrow$$
$$NaNO_3 \quad H_2O$$
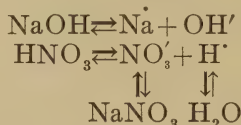
The H and OH' ions unite to form un-ionized water, but the $\overset{.}{Na}$ and NO'_3 ions unite scarcely at all, especially if the solutions are dilute. The same is true when other strong acids and bases are employed; that is, in solution practically the only reaction is the formation of water. Hence the neutralization of an acid by a base is due almost entirely to the following reaction:[1]

$$\overset{.}{H} + OH' \rightarrow H_2O.$$
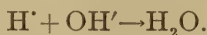
If two highly ionized substances are mixed which give rise to a

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[1] Further evidence of this is afforded by the fact that when chemical equivalents of any strong base and strong acid are united, the same quantity of heat, viz., 13,700 cal., is liberated.

weak acid or base, the reaction goes forward for a similar reason. Potassium cyanide and sulphuric acid react as follows:

$$2KCN \rightleftarrows 2K^{\cdot} + 2CN'$$
$$H_2SO_4 \rightleftarrows SO_4'' + 2H^{\cdot}$$
$$\Updownarrow \qquad \Updownarrow$$
$$K_2SO_4 \quad 2HCN$$
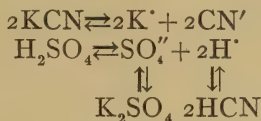
Practically the only action here is the formation of the slightly ionized HCN (see p. 79) thus,

$$H^{\cdot} + CN' \longrightarrow HCN.$$
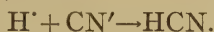
DISSOCIATION IN STEPS. Polybasic acids ionize in steps. Taking phosphoric acid, H_3PO_4, for example, in a normal solution it is about 8% ionized, and this results for the most part from a separation into $H^{\cdot}$ and $H_2PO'_4$. If the solution is partially neutralized so that $H^{\cdot}$ ions are removed, the second $H^{\cdot}$ ion begins to dissociate, and finally, if the addition of base is continued, the third $H^{\cdot}$ ion begins to separate. Hence the dissociation of the acid goes through the following steps:

$$H_3PO_4 \leftrightarrows H^{\cdot} + H_2PO'_4, \ H_2PO'_4 \leftrightarrows H^{\cdot} + HPO_4'', \ HPO_4'' \leftrightarrows H^{\cdot} + PO_4'''.$$
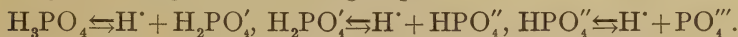
This does not mean that the first of these reactions goes to completion before the others begin, because they are all interdependent and the equilibrium in any one is affected by the concentration of the ions in the others. A solution of phosphoric acid contains some of all the ions mentioned. In the case of sulphuric acid, which is about 50% dissociated in a normal solution, probably about 90% of the $H^{\cdot}$ ions present result from the reaction: $H_2SO_4 \rightleftarrows H^{\cdot} + HSO'_4$, and the remaining 10% from the reaction: $HSO'_4 \leftrightarrows H^{\cdot} + SO_4''$.

REPRESSION OF IONIZATION. If to a solution of an electrolyte is added another electrolyte with a common ion, so that the concentration of the common ion is increased, the degree of dissociation of the first electrolyte is diminished. This is a direct result of the law,

p. 2, and its formulation in Equation (2), viz. $\dfrac{c_1 c_2}{c} = K$. For this increases the concentration of c_1, and hence c increases and c_2 diminishes in order to preserve the constancy of K. If the

electrolyte is a weak acid or base its ionization may be reduced practically to zero by this process. By adding solid sodium acetate to a normal solution of acetic acid until the concentration of the salt is normal, the degree of ionization of the acid is reduced from 0.004 (p. 79) to 0.00003. This follows directly from the equation, which may be written in the form $c_1c_2 = cK$. In a normal solution $c = 0.996$, and as the ionization of the acid becomes less during the process just mentioned, the value of c lies between 0.996 and 1.000. This means that it is practically constant and equal to 1, and therefore $c_1c_2 = K = 0.000016$.[1] The degree of ionization of sodium acetate in a normal solution is 0.53. Hence $c_2 = \dfrac{0.000016}{0.53} = 0.00003$. The concentration of the H$^\cdot$ ions in such a solution can therefore be made as small as desired.

The degree of ionization of the stronger acids is somewhat affected by the addition of a salt with a common ion, but relatively this effect is slight.   Such an acid is usually fully as much ionized as its salts, so that by adding a salt until the concentration of the salt equals that of the acid the concentration of the common ion is no more than doubled. This does not reduce to one-half of its former value the concentration of the H$^\cdot$ ions, for the concentration of the un-ionized portion is considerably affected and a new equilibrium reached but little different from the former.[2]

If it is desired to diminish the concentration of the H$^\cdot$ ions in the solution of a strong acid without neutralizing with a base, it may usually be accomplished by adding to the solution sodium or ammonium acetate in excess. In case the solution contained hydrochloric acid, the formulation of the reaction would be as follows:

$$HCl \rightleftharpoons H^\cdot \quad + \quad Cl'$$
$$NaC_2H_3O_2 \rightleftharpoons C_2H_3O_2' + Na.$$
$$\Updownarrow \qquad \Updownarrow$$
$$HC_2H_3O_2 \quad NaCl$$
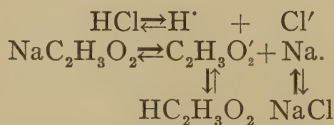
The H$^\cdot$ ions are removed by the formation of the little ionized

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[1] In a normal solution of acetic acid $c_1 = c_2 = 0.004$.

[2] This readily follows from the nature of the equilibrium equation, $\dfrac{c_1c_2}{c} = K$.

acetic acid, and the dissociation of the acetic acid is greatly repressed by the excess of sodium acetate present. Advantage is frequently taken of this method of reducing the concentration of H˙ ions in many of the operations of Qualitative Analysis.

EQUILIBRIUM IN A SATURATED SOLUTION. In a saturated solution the solid solute is in equilibrium with the dissolved solute. If the solute is an electrolyte, it is partially dissociated into its ions, but the equilibrium just referred to is between the solid and the undissociated portion of the solute. In addition to this there is the further equilibrium existing between the ions and the undissociated portion. Thus for sodium chloride in a saturated solution we have,

$$NaCl \text{ (solid)} \rightleftharpoons NaCl \text{ (disslv'd)} \rightleftharpoons \overset{.}{Na} + Cl'.$$
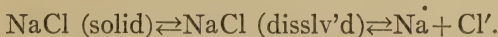
Anything which disturbs this equilibrium at one point will disturb it throughout. Now, we know that the addition of a substance with a common ion will repress the dissociation and produce more un-ionized salt. But more un-ionized salt cannot exist in the solution because it is saturated, and therefore the un-ionized portion formed will fall out as a precipitate. In this way the total solubility of the salt is decreased. Consequently, if secondary reactions do not occur, an electrolyte is less soluble in the presence of a substance having a common ion than in the pure solvent. For example, sodium chloride is much less soluble in a solution of hydrochloric acid than in water.

THE SOLUBILITY PRODUCT. We have here the same equilibrium existing between the soluble portion of the electrolyte as formerly, viz., $c_1 c_2 = cK$. In a saturated solution, however, it has been shown that c is constant, and hence $c_1 c_2$ is constant, and we write,

$$c_1 c_2 = s.[1] \tag{3}$$

This quantity indicated by s is called the solubility product of the substance. In the example just cited when hydrochloric acid is added to a saturated solution of sodium chloride, the concentration, c_2, of the Cl' ions is increased. But since the product, $c_1 c_2$,

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[1] Mathematically, this equation does not hold in all cases, but the general principles to be developed from it hold within certain limits, so that they are of great value in analytical work.

must remain constant, more un-ionized NaCl is formed and at once precipitated, so that the concentration of the Na ions, c_1, and consequently also that of the total dissolved sodium chloride, is greatly diminished.

The following principles have been found to apply with reference to the solubility product:

1. **Precipitation of an electrolyte will occur only when its solubility product is exceeded.**

2. **Any process which permanently decreases the solubility product of an electrolyte, already precipitated, will cause it to dissolve.**

PRECIPITATION. The first principle may be illustrated by adding to a solution of calcium chloride, ammonium oxalate solution. Calcium oxalate is a rather insoluble substance, and its solubility product is therefore small and is soon exceeded, so that a precipitate of this substance is obtained. The formulation of the reaction is:

$$CaCl_2 \rightleftharpoons Ca^{\cdot\cdot} + 2Cl'$$
$$(NH_4)_2C_2O_4 \rightleftharpoons C_2O_4'' + 2NH_4^{\cdot}$$
$$\text{(disslv'd) } CaC_2O_4 \quad 2NH_4Cl$$
$$\text{(insol.) } CaC_2O_4$$
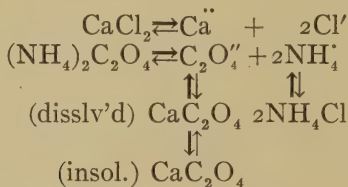
If equivalent quantities of these substances were first mixed, and then more ammonium oxalate solution added, c_2, the concentration of the C_2O_4'' ions, is increased, and consequently more CaC_2O_4 will precipitate and c_1, the concentration of the Ca ions remaining in the solution, be diminished. Theoretically, therefore, the greater the excess of the precipitating agent the more complete will be the precipitation. In actual practice, however, it is usually best to employ only a moderate excess. Frequently secondary reactions may result which neutralize the advantages just mentioned, and also, in case the filtrate is to be used, a great excess of the precipitant may cause serious complications.

SOLUTION. The second principle may be illustrated by the solubility of silver chloride in ammonia. For precipitated silver chloride we have the equilibrium:

$$AgCl \text{ (insol.)} \leftrightharpoons \underset{c}{AgCl} \text{ (disslv'd)} \rightleftharpoons \underset{c_1}{\overset{\cdot}{Ag}} + \underset{c_2}{Cl'}$$
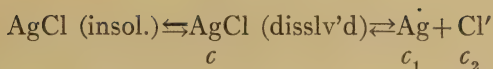
If ammonia is added to this precipitate some $Ag(NH_3)_2Cl$ is formed, whose ions are $Ag(NH_3)_2^{\cdot}$ and Cl'. (The ion $Ag(NH_3)_2^{\cdot}$ dissociates further very slightly, giving exceedingly few $\overset{\cdot}{Ag}$ ions.) By this action the concentration, c_1, of the $\overset{\cdot}{Ag}$ ions in the solution is diminished so that $c_1 c_2 < s_{AgCl}$; AgCl therefore dissolves to restore the equilibrium, and this is consumed in turn to form more of the complex ion $Ag(NH_3)_2^{\cdot}$ until all of the precipitate has dissolved.

Calcium oxalate is dissolved by an excess of hydrochloric acid. The formulation of the reaction is as follows:

$$CaC_2O_4 \rightleftharpoons \underset{\text{(dissl'vd)}}{CaC_2O_4} \rightleftharpoons \overset{\cdot\cdot}{Ca} + C_2O_4''$$
$$\underset{\text{(insol.)}}{}$$
$$2HCl \rightleftharpoons 2Cl' + 2H^{\cdot}$$
$$\Updownarrow \qquad \Updownarrow$$
$$CaCl_2 \quad H_2C_2O_4$$
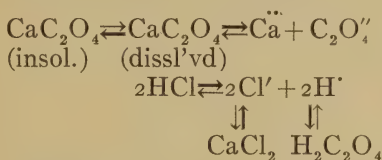
The $H_2C_2O_4$ is but little ionized, and in the presence of the great concentration of $H^{\cdot}$ ions from the excess of HCl, its ionization is still further repressed, so that it supplies fewer C_2O_4'' ions to the solution than does a saturated solution of CaC_2O_4. The result, therefore, is that the equilibrium is displaced toward the right and the CaC_2O_4 dissolves. Acetic acid supplies so few $H^{\cdot}$ ions that in its presence the ionization of $H_2C_2O_4$ is not appreciably repressed, and, therefore, the concentration of the C_2O_4'' ions would exceed the concentration in a saturated solution of CaC_2O_4. Acetic acid and other weak acids will therefore not dissolve precipitates of this class. (BaCrO$_4$ belongs to this class; see p. 48.)

This principle also applies to the solubility of magnesium hydroxide in ammonium chloride solution. If to a solution of magnesium chloride is added ammonium hydroxide solution, some magnesium hydroxide is precipitated. The formulation of the reaction is as follows:

$$MgCl_2 \rightleftharpoons \overset{\cdot\cdot}{Mg} + 2Cl'$$
$$2NH_4OH \rightleftharpoons 2OH' + 2NH_4^{\cdot}$$
$$\Updownarrow \qquad \Updownarrow$$
$$\text{(disslv'd) } Mg(OH)_2 \quad 2NH_4Cl$$
$$\Updownarrow$$
$$\text{(insol.) } Mg(OH)_2$$
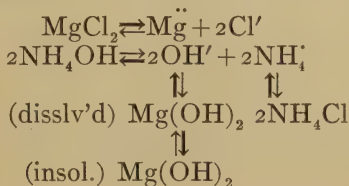
NH_4OH is but little ionized, but nevertheless the solubility product of $Mg(OH)_2$ is exceeded and a precipitate is therefore obtained. The simultaneous formation of NH_4Cl, which is highly ionized, increases the concentration of the $NH_4^{\cdot}$ ions in the solution, and hence represses the ionization of the NH_4OH to such an extent that the solubility product of $Mg(OH)_2$ is soon no longer exceeded and the precipitation remains incomplete. If now ammonium chloride is added to the magnesium chloride solution in the first place, then when ammonium hydroxide is added no precipitate of $Mg(OH)_2$ is obtained; for the ionization of the NH_4OH is so repressed by the great concentration of the $NH_4^{\cdot}$ ions present, that the solubility product of $Mg(OH)_2$ is not reached at all.

HYDROLYSIS. Water is slightly ionized (1 part in 10 million at 18°) into $H^{\cdot}$ and OH' ions. Even this extremely small concentration of these ions is, however, sufficient to disturb the ionic equilibrium of many salts, giving rise to noticeable reactions. Such reactions are called hydrolytic reactions, or simply hydrolysis.

Salts of strong acids with strong bases are not appreciably affected in this manner, but salts either of a weak acid, of a weak base, or of both suffer quite noticeable decomposition. If the salt is one of a weak acid with a strong base, as KCN, the reaction taking place may be thus formulated:

$$KCN \rightleftharpoons K^{\cdot} + CN'$$
$$H_2O \rightleftharpoons OH' + H^{\cdot}$$
$$\qquad \updownarrow \qquad \updownarrow$$
$$\qquad KOH \quad HCN$$
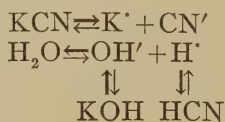
HCN is but little ionized (0.0001 in normal solution), and therefore in the presence of a relatively high concentration of CN' ions, as here its ionization is strongly repressed, so that it is of the same order as that of water itself. This slight ionization of the HCN causes the equilibrium to shift toward the right, more water is ionized, and a new equilibrium is finally established. This process causes an increase in the concentration of the OH' ions, since KOH is highly ionized. Solutions of such salts therefore always react alkaline.

If the salt is one of a strong acid with a weak base, hydrolysis occurs either on account of the slight degree of ionization of the base or on account of its extremely small solubility. Taking ferric chloride as an example, the reaction may be represented thus:

$$FeCl_3 \rightleftharpoons \overset{\cdots}{Fe} + 3Cl'$$
$$3H_2O \leftrightharpoons 3OH' + 3H^{\cdot}$$
$$\Updownarrow \qquad \Updownarrow$$
$$Fe(OH)_3{}^1 \quad 3HCl$$
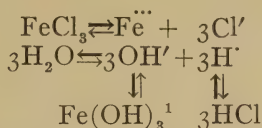
On account of the slight dissociation of ferric hydroxide, the equilibrium is displaced toward the right, the ferric hydroxide being either precipitated or remaining in solution in the colloidal state. $H^{\cdot}$ ions are produced by the action, which, on account of the high degree of ionization of HCl, remain free and give the solution an acid reaction.

If the salt is one of a weak acid with a weak base, hydrolysis takes place in a similar manner, but decomposition into the constituent acid and base is commonly much more complete. The precipitation of the basic acetates of iron, aluminium and chromium in the Iron group, p. 40, affords an example of this.

Both rise in temperature and increase in the dilution of the solution favor hydrolysis. The hydrolysis of ammonium chloride, which cannot be detected by simple means at ordinary temperature, is easily shown to occur at 100°. This effect of high temperature and of dilution are taken advantage of in the precipitation of the Iron group just referred to.

One principle which must not be lost sight of in connection with hydrolysis is that in any aqueous solution the product of the concentrations of the $H^{\cdot}$ and OH' ions is constant at constant temperature. This follows at once from the equilibrium equation for the ionization of water, viz.:

$$\underset{c}{H_2O} \rightleftharpoons \underset{c_1}{H^{\cdot}} + \underset{c_2}{OH'},$$
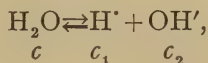
whence $c_1 c_2 = cK$. Since c, the concentration of the undissociated water in any aqueous solution, is practically constant, $c_1 c_2 =$ constant. This constant at any temperature can be calculated from

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[1] It is more probable that basic chlorides of iron are produced in this reaction, but for the sake of simplicity, we assume that the hydroxide is formed.

the degree of ionization of water at that temperature.   At 18°
it is 1×10^{-12}.   From this one can calculate the concentration of
either the $H^{\cdot}$ or the OH' ions in a solution, provided that the con-
centration of the other is known.   For example, in a decinormal
solution of acetic acid the concentration of the $H^{\cdot}$ ions is about
0.01.   The concentration of the OH' ions in this solution is
therefore 1×10^{-10}.

AMPHOTERIC
ELECTROLYTES.
Some substances may function either as an acid
or as a base, and are for this reason known as
amphoteric electrolytes.   In inorganic chemistry
this class of substances is confined to a few
metallic hydroxides, as $Zn(OH)_2$ and $Al(OH)_3$.   They are almost
insoluble in water, the small portion that is in solution undergo-
ing ionization either as an acid or as a base.   The equilibrium
with $Zn(OH)_2$ in contact with water may be represented thus:

$$Zn(OH)_2 (\text{insol.})$$
$$\Updownarrow$$
$$2H^{\cdot} + ZnO_2'' \rightleftharpoons Zn(OH)_2 \rightleftharpoons \ddot{Z}n + 2OH'$$
$$(\text{disslv'd})$$
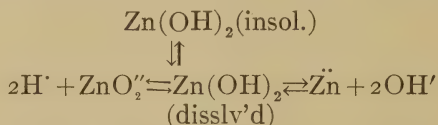
In the presence of an acid, the $H^{\cdot}$ ions repress the dissociation
toward the left, the dissociation toward the right thereby tends to
become more prominent, the $H^{\cdot}$ ions at the same time combining
with the OH' ions to form un-ionized water, thus favoring a
shifting of the equilibrium toward the right.   In this case there-
fore the substance acts as a base.   In the presence of a base,
especially the stronger ones, as $NaOH$, etc., the OH' ions repress
the dissociation toward the right and favor that toward the left;
hence the substance acts as an acid (see 4c, p. 42, and 5f, p. 44).
With weak bases, as NH_4OH, that are not ionized to a much
greater extent than the substance itself, it commonly acts neither
as an acid nor as a base.

ELECTRO-
MOTIVE
SERIES.
The relative tendency of the metals and hydro-
gen to pass from the free into the ionic condition
is indicated in the following table.   This
tendency is greatest with potassium and least
with gold.   This arrangement is known as the
electromotive series, for the reason that the electromotive force
required to separate these elements from normal solutions of

Potassium
Sodium
Lithium
Barium
Strontium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Cadmium
Iron
Cobalt
Nickel
Tin
Lead
Hydrogen
Arsenic
Copper
Antimony
Bismuth
Mercury
Silver
Palladium
Platinum
Gold

their salts decreases in the order in which they are given. Any element in the table will displace the ions of any of the elements below it from solution; for example, calcium metal will displace $\overset{..}{Zn}$ ions from solutions of zinc salts, thus:

$$ZnCl_2$$
$$\updownarrow$$
$$\overset{..}{Zn} + Ca \rightarrow \overset{..}{Ca} + Zn$$
$$+ \qquad +$$
$$2Cl' \rightarrow 2Cl'$$
$$\updownarrow$$
$$CaCl_2$$
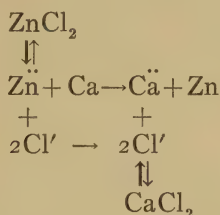
Or since both salts are quite completely ionized in dilute solution, the principal reaction is,

$$Ca + \overset{..}{Zn} \rightarrow Zn + \overset{..}{Ca}.$$

The position of hydrogen in the series is of special importance. Only the metals above it will displace it from the ionic state; that is, from dilute acids. Acids will therefore dissolve only those metals above hydrogen and not those below. The latter are, however, attacked by suitable oxidizing agents. It must be remembered that nitric acid acts as an oxidizing agent in addition to functioning as an acid, which accounts for its power to dissolve the metals from arsenic to silver, inclusive. The metals below silver are attacked only by more powerful oxidizing agents, as nascent chlorine.

OXIDATION
AND
REDUCTION.

Oxidation is the process in which oxygen or some non-metallic element is added to, or hydrogen or some metallic element removed from, a substance. Reduction always accompanies oxidation. It is the reverse of this; that is, the process in which oxygen or some non-metallic element is removed from, or hydrogen or some metallic element added to, a substance.

In the following examples the oxidizing agent is written first; during the action it is reduced:

$$2HgCl_2 + SnCl_2 \rightarrow 2HgCl + SnCl_4,$$
$$Cl_2 + 2K_4Fe(CN)_6 \rightarrow 2KCl + 2K_3Fe(CN)_6.$$
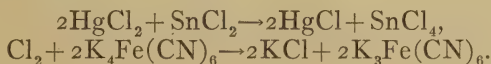
These reactions take place in solution. When, therefore, we write the reaction in the ionic form omitting ions common to both sides, we have,

$$2\overset{..}{Hg}+\overset{..}{Sn}\longrightarrow 2\overset{.}{Hg}+\overset{....}{Sn},^{1}$$
$$Cl_2+2Fe(CN)_6''''\longrightarrow 2\overset{.}{Cl}'+2Fe(CN)_6'''.$$
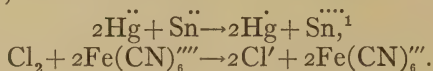
According to this, then, we see that oxidation results in an increase in the positive charge or a decrease in the negative charge, and reduction in the decrease in the positive charge or increase in the negative.

In the case of many complex reactions of oxidation and reduction when written in the ionic form, the application of the rule above is not apparent; the first rule should, therefore, be used as a criterion in such cases. The following reactions are written first in the molecular and then in the ionic form:

(1) $2FeCl_3+H_2S\longrightarrow 2FeCl_2+2HCl+S,$ (a)

$2K_2CrO_4+10HCl+3H_2S\longrightarrow 2CrCl_3+4KCl+8H_2O+3S,$ (b)

$HNO_3+3HCl+3FeCl_2\longrightarrow NO+2H_2O+3FeCl_3,$ (c)

$3Na_2O_2+2Cr(OH)_3\longrightarrow 2H_2O+2NaOH+2Na_2CrO_4,$ (d)

$2K_2CrO_4+2H_2SO_4+3H_2SO_3\longrightarrow Cr_2(SO_4)_3+2K_2SO_4+5H_2O,$ (e)

(2) $2\overset{.}{Fe}+\overset{..}{S}''\longrightarrow 2\overset{.}{Fe}+S,$ (a)

$(2CrO_4''+16\overset{.}{H})+3\overset{..}{S}''\longrightarrow (2\overset{..}{Cr}+8H_2O)+3S,$ (b)

$(NO_3'+4\overset{.}{H})+3\overset{.}{Fe}\longrightarrow (NO+2H_2O)+3\overset{..}{Fe},$ (c)

$3\overset{..}{O_2}+2\overset{..}{Cr}+4OH'\longrightarrow 2H_2O+2CrO_4'',$ (d)

$2CrO_4''+10\overset{.}{H}+3SO_3''\longrightarrow 2\overset{..}{Cr}+5H_2O+3SO_4''.$ (e)
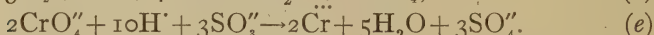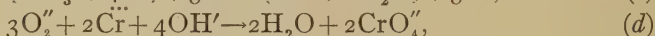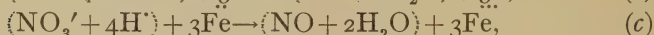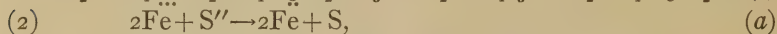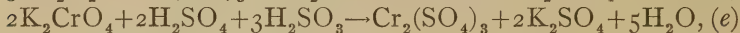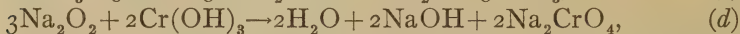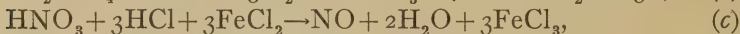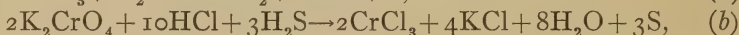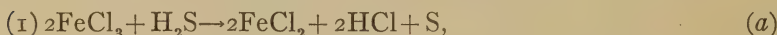
In (2), reaction (a) easily corresponds to the definition for ionic oxidation and reduction. Reactions (b) and (c) also do, if we consider the groups within the dotted parentheses as a whole. For example, $(2CrO_4''+16\overset{.}{H})$ loses six positive charges, and is therefore reduced; while $3S''$ loses six negative charges, and hence is oxidized. Reactions (d) and (e) do not fulfill the conditions of the definition in the form in which they stand. Students should, however, for the sake of experience try to express in the ionic form all reactions of oxidation and reduction taking place in solution. When the reaction is not between substances in solution only the molecular reaction should be written (see the test for manganese, 5g, p. 45).

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[1] Any ionic reaction written in this form must have the same excess of positive or the same excess of negative charges on each side of the equation.

DIRECTIONS FOR LABORATORY WORK.

The student should keep complete notes of all procedure and results, and should be required to write the equations for reactions both in the ordinary molecular form and also in the ionic form in case the reaction takes place in solution. (See the preceding pages for examples.) The notes in connection with every procedure (usually on the opposite page) should be read and understood before beginning the manipulation.

BASIC ANALYSIS.

1. As an exercise in separating the cations into groups use a solution containing $AgNO_3$, $Cu(NO_3)_2$, $Fe(NO_3)_3$, $Zn(NO_3)_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, and KNO_3. Go through the operations indicated on pp. 24, 28, 40, 43, 46 and 50.

2. For the precipitation and separation of the cations of the Silver group use a solution containing $AgNO_3$, $HgNO_3$,[1] and $Pb(NO_3)_2$, and proceed according to the directions given on pp. 24 and 26.

3. Take a solution of $BiCl_3$ and $SbCl_3$ in excess of HCl and precipitate the Copper-Tin group as directed on p. 28. Then separate the Copper group from the Tin group according to the directions on p. 30.

4. For the precipitation and separation of the cations of the Copper group use a solution of $HgCl_2$, $PbCl_2$, $BiCl_3$, $CuCl_2$, and $CdCl_2$. Proceed as in 3, and in addition carry out the processes indicated on p. 32.

5. For the precipitation and separation of the cations of the Tin group use a solution of $AsCl_3$,[2] $SbCl_3$, and $SnCl_2$. Proceed as in 3, and in addition carry out the processes indicated on pp. 34–5.

6. Before beginning the separation of the Iron group the following experiments illustrating the behavior of phosphates and oxalates should be made (first read carefully pp. 37–39):

(a) To a solution of $CaCl_2$ add sodium phosphate solution, shake and divide into two unequal portions without filtering.

[1] Free mercury must always be present in the stock bottle containing this solution.
[2] This solution is prepared by boiling As_2O_3 with dilute HCl.

Treat the smaller portion with acetic acid and the larger portion with hydrochloric acid. Divide the latter into two portions. Just neutralize one with NH_4OH. Add an equal volume of $4N$ $NH_4C_2H_3O_2$ to the other, and shake thoroughly (see p. 5).

(b) Treat $CaCl_2$ solution with ammonium oxalate solution, and proceed in exactly the same manner with the precipitate as with the precipitate of calcium phosphate in (a).

7. Take a solution of $FeSO_4$, $Al_2(SO_4)_3$ and $Cr_2(SO_4)_3$ to illustrate the precipitation and separation of the cations of the Iron group. Make first preliminary tests 3, p. 22, and then proceed according to the directions, pp. 40 and 42.

8. For the precipitation and separation of the cations of the Zinc group use a solution of $CoCl_2$, $NiCl_2$, $ZnCl_2$, and $MnCl_2$. Proceed according to the directions, pp. 43 and 44.

9. To illustrate the precipitation and separation of the cations of the remaining groups take a solution of $CaCl_2$, $SrCl_2$, $BaCl_2$, $MgCl_2$, KCl, $NaCl$, $LiCl$, and NH_4Cl. First make preliminary tests 1 and 2, p. 22, and then proceed according to the directions, pp. 46, 48 and 50.

10. After completing each one of the foregoing exercises (except 6), "unknown" solutions may be given out containing the cations of any of the groups preceding. For example, after finishing 7, a solution may be given out containing $HgNO_3$, $Hg(NO_3)_2$, $Cd(NO_3)_2$,[1] $Fe(NO_3)_3$, and $Al(NO_3)_3$, with instructions to make preliminary tests 3 and 4, p. 22, and then proceed with the precipitation and separation of the groups so far covered.

After completing 9, a solution may be given out containing any of the cations with instructions to make, hereafter, all of the preliminary tests, p. 22.

ACID ANALYSIS.

11. Use the following substances for test 1, p. 53: Na_2SiO_3, Na_2SO_3, $Na_2S_2O_3$, Na_2CO_3, $(NH_4)_2C_2O_4$, $Na_2C_4H_4O_6$, $NaC_2H_3O_2$, $NaCl$, KBr, KI, CaF_2, KCN, PbS, KNO_3, KNO_2, $KClO_3$, and $CaOCl_2$.

---

[1] When a member of the Silver group is present, members of the Tin group cannot be added without producing a precipitate, as excess of HCl is required to hold the latter in solution.

12. Use the following for test 2, p. 54: Solutions of $Na_2S_2O_3$, Na_2SO_4, K_2CrO_4, and Na_2HPO_4.

13. Use for test 3, p. 55, the following: Solutions of NaCl, KBr, KI, KCN, and K_2S. With these solutions omit 3(B). With solutions of the substances of 12 do 3(B), acidifying first with HNO_3 as in 3(A).

Now mix solutions of KI and Na_2HAsO_4, and make both tests 3(A) and(B).

14. Using, as the case may be, solid substances or the proper solutions, make the special tests, pp. 57–65.

15. A few mixtures of solid salts of sodium, potassium or ammonium should then be given out for practice in identifying the anions, as, for example, a mixture of Na_2HPO_4, KCN, and KNO_3.

First make general test 1. Then dissolve some of the mixture in water and make tests 2, 3(A) and (B). From the information thus gained make special tests for those anions not shown to be absent by the general tests.

DRY SUBSTANCES.

16. Make the closed-tube test, p. 66, with the following substances: $Ni(NO_3)_2$, $Na_2C_4H_4O_6$, $KClO_3$, $BiONO_3$, $HgCl$, NH_4Cl, FeS_2, $ZnSO_4$.

17. Make the test on charcoal with the blowpipe, p. 68, with the following substances: NaCl, $KClO_3$, As_2O_3, ZnO, $CuSO_4$, $BiONO_3$, PbS.

18. Make the bead test, p. 69, with the following substances: $CuSO_4$, $Cr_2(SO_4)_3$, $FeSO_4$, MnO_2, Na_2SiO_3. The last-named substance should be treated as directed in the note.

19. The flame tests are probably already sufficiently familiar. If not, carry out the test, p. 69, with the chlorides of the metals mentioned.

20. Various mixtures of salts, industrial products, or alloys should then be given out for analysis. (The first few mixtures should not contain substances insoluble in acids. For the treatment of alloys see p. 74.)

With substances other than alloys the student should proceed as follows:

2

(*a*) Make the dry tests, pp. 66–69, and test 1, p. 53.

(*b*) Prepare the solution for the Basic Analysis according to p. 70 *et seq.*   Proceed with the analysis of the solutions obtained exactly as in Exercise 10 (last part), except that the tests for interfering substances, p. 37, must be made.

(*c*) During the progress of the Basic Analysis any opportunity should be improved to prepare the solution for the Acid Analysis according to pp. 74–75.

(*d*) Make the preliminary tests for anions, pp. 54–56, and then the special tests, pp. 57–65.

BASIC ANALYSIS.

Basic analysis has to do with the separation and identification of the metals and metallic radicals, or, since most of the reactions concerned in these processes take place in solution, of the positive ions or cations. About one-half of the known metals occur so rarely that it is not worth while to include them in an elementary course of Qualitative Analysis. Twenty-three metals and the group NH_4 remain to be considered. Many of these exhibit more than one valence even when functioning as a metal, so that the number of cations somewhat exceeds the above number. These ions are: $\overset{.}{Ag}$, $\overset{..}{Hg}$, $\overset{.}{Hg}$, $\overset{..}{Pb}$, $\overset{...}{Bi}$, $\overset{..}{Cu}$, $\overset{..}{Cd}$, $\overset{...}{As}$, $\overset{.....}{As}$, $\overset{...}{Sb}$, $\overset{.....}{Sb}$, $\overset{..}{Sn}$, $\overset{....}{Sn}$, $\overset{..}{Fe}$, $\overset{...}{Fe}$, $\overset{...}{Al}$, $\overset{...}{Cr}$, $\overset{..}{Ni}$, $\overset{..}{Co}$, $\overset{..}{Mn}$, $\overset{..}{Zn}$, $\overset{..}{Ca}$, $\overset{..}{Sr}$, $\overset{..}{Ba}$, $\overset{..}{Mg}$, $\overset{.}{Na}$, $\overset{.}{K}$, $\overset{.}{Li}$, NH_4.

As an aid to their ultimate identification these ions are first separated into groups by means of certain reagents (L. C., p. 370; S. C., p. 440). Subsequently they are separated from the other members of the same group and identified. The different groups are characterized as follows:

Silver Group.

Ions uniting with the Cl' to form insoluble chlorides: $\overset{.}{Ag}$, $\overset{.}{Hg}$, $\overset{..}{Pb}$.

Copper-Tin Group.

Ions uniting with the S'' to form sulphides insoluble in dilute mineral acids:[1] $\overset{..}{Hg}$, $\overset{..}{Pb}$,[2] $\overset{..}{Cu}$, $\overset{..}{Cd}$, $\overset{...}{Bi}$, $\overset{...}{As}$, $\overset{.....}{As}$, $\overset{...}{Sb}$, $\overset{.....}{Sb}$, $\overset{..}{Sn}$, $\overset{....}{Sn}$.

Iron Group.[3]

Ions forming basic acetates insoluble in dilute acetic acid: $\overset{...}{Fe}$,[4] $\overset{...}{Al}$, $\overset{...}{Cr}$.

Zinc Group.

Ions uniting with the S'' to form sulphides insoluble in alkaline solution: $\overset{..}{Ni}$, $\overset{..}{Co}$, $\overset{..}{Mn}$, $\overset{..}{Zn}$.

---

[1] In connection with this group and each of the following, the phrase *after the ions of the preceding groups have been removed* is to be understood. For example, the ions of the Silver group, unless previously removed, form sulphides insoluble in dilute acids, the same as the ions of the Copper-Tin group.

[2] For the occurrence of $\overset{..}{Pb}$ here as well as in the Silver group, see Note 2, p. 25.

[3] For optional method of procedure with this and the following group see p. 80 et seq.

[4] $\overset{..}{Fe}$ is oxidized to $\overset{...}{Fe}$, so that all the iron will be precipitated here.

Calcium Group.

Ions uniting with the CO_3'' to form carbonates insoluble in ammonia: $\overset{..}{Ca}$, $\overset{..}{Sr}$, $\overset{..}{Ba}$.

Magnesium.

Whose ion unites with the PO_4''' to form a phosphate insoluble in ammonia: $\overset{..}{Mg}$.

Potassium Group.

Ions which unite with none of the more commonly occurring anions to form insoluble compounds: $\overset{.}{Na}$, $\overset{.}{K}$, $\overset{.}{Li}$, $\overset{.}{NH}_4$.

PRELIMINARY TESTS.

Any solution submitted by the instructor, or prepared from a solid substance by the student (see p. 70), for the Basic Analysis will be called throughout the following the **original solution.**

In such solutions the following tests should be made before beginning the separation into groups. The reasons for this are given in the notes on the opposite page.

1. *Test for Ammonium, $NH_4^{\cdot}$.*

Place some of the solid substance or the original solution in a small beaker, add concentrated NaOH until alkaline, and cover quickly with a clean watch-glass, on the under side of which is a piece of moist red litmus-paper. Warm gently (do not boil). If the litmus turns blue, place it where it will dry. The return of the red color indicates the presence of ammonium salts.

The following tests are best made in an acid solution. Therefore, either acidify a small portion of the original solution with HCl or, better, use a small portion of the filtrate from the Silver group for the tests.

2. *Test for Sodium, $N\overset{\cdot}{a}$.*

Dip a clean platinum wire into the solution and hold it in the Bunsen flame. A persistent, intensely yellow flame indicates sodium. This may be omitted in case a similar tests has been made with the solid substance (see p. 69).

3. *Test for the Condition of Iron, $F\overset{..}{e}$ or $F\overset{...}{e}$.*

To a small portion of the acidified solution, which has been considerably diluted, add a few drops of freshly prepared $K_3Fe(CN)_6$. A deep blue precipitate, $Fe_3(Fe(CN)_6)_2$ (Turnbull's blue), indicates the presence of $F\overset{..}{e}$.

To another small portion of the acidified solution likewise diluted add a few drops of freshly prepared $K_4Fe(CN)_6$. A deep blue precipitate, $Fe_4(Fe(CN)_6)_3$ (Prussian blue), indicates the presence of $F\overset{..}{e}$.

(A solution of KSCN may be used for the last test. If $F\overset{...}{e}$ is present a red color due to $Fe(SCN)_3$ will be obtained.)

4. *Test for the Condition of Tin, $S\overset{..}{n}$ or $S\overset{....}{n}$.*

Add a few drops $HgCl_2$ to a small portion of the dilute acidified solution, shake, and let stand a few moments. A white precipitate, HgCl, or a gray one, Hg, indicates the presence of $S\overset{..}{n}$.

If this test results negatively and tin is subsequently found in the Tin group, the original solution contained $S\overset{...}{n}$.

NOTES ON THE PRELIMINARY TESTS.

1. It is necessary to test for NH_4^+ here, as ammonium salts are added to the solution in the course of the separation into groups.

2. If the litmus-paper turns blue but does not return to its red color on drying, it shows that through unskillful manipulation some of the non-volatile alkali, $NaOH$, came in contact with the paper. The test is therefore undecisive and should be repeated.

3. Sodium compounds are present in minute quantities everywhere. Delaying the test for this element, therefore, until the Potassium group may result in the accumulation of sufficient $\overset{.}{Na}$ (present in the reagents as an impurity) in the solution to make the test doubtful. Even when made at this early stage of the analysis, the flame must not only be yellow, but the yellow color must persist for some time to warrant reporting the presence of $\overset{.}{Na}$.

4. Ferric iron is reduced to ferrous on passing H_2S through the solution, hence the necessity for making the tests for these ions before proceeding to the precipitation of the Copper-Tin group. Furthermore, ferrous iron is oxidized to ferric before precipitating the Iron group.

For a discusson of the iron cyanides, see L. C., p. 360; S. C., pp. 501–2.

5. Various other cations also give precipitates with the iron-cyanides, but none give dark blue precipitates except $\overset{..}{Fe}$ and $\overset{...}{Fe}$. Even in the presence of colored ions, as $\overset{..}{Cu}$, $\overset{..}{Co}$, $\overset{..}{Ni}$ and $\overset{...}{Cr}$, no ambiguity should arise especially in case the solution is dilute. $Cu_3[Fe(CN)_6]_2$ is light green, and $Co_2Fe(CN)_6$ is green or very light blue. These are the ones most nearly like the iron precipitates.

6. The tin ions are reduced to metallic tin before their final identification in the Tin group; hence there is no provision made for distinguishing between them at that point. This necessitates the preliminary test given here.

7. An element may be identified in three ways: (1) by its isolation; (2) by causing it to form some characteristic compound; (3) by causing it to produce a change in some other substance. The test for tin is one of the third class (see L. C., p. 338; S. C., p. 437).

PRECIPITATION OF THE SILVER GROUP.

1. To the original solution add one-tenth its volume of $8N$ HCl, shake thoroughly, filter, and wash with cold water until practically free from acid.[1]

Precipitate:	Filtrate:[2]
$AgCl$, $HgCl$, $PbCl_2$. Analyze according to directions on p. 26.	Ions of the following groups: $\overset{..}{Hg}$, $\overset{..}{Cu}$, etc. Proceed to the precipitation of the Copper-Tin group, p. 28.

[1] The first wash-water may be allowed to run through into the filtrate; subsequent ones should be thrown away.

[2] To every filtrate should be added at once a few drops of the precipitating agent, in this case HCl, to insure that precipitation has been complete. If more of the precipitate falls, more of the reagent should be added and filtration repeated. This should be continued until addition of the reagent produces no further precipitation. *This precaution should never be omitted,* even in the absence of specific directions. It is one of the two principal sources of error in analytical work, the other being *insufficient washing of precipitates.*

NOTES ON THE PRECIPITATION OF THE SILVER GROUP.

1. The solution should be neutral or acid before adding HCl. The addition of HCl to some alkaline solutions may produce precipitates very different from those mentioned here. As an example see the reprecipitation of the sulphides of the Tin group on acidifying with HCl, p. 30 (*d*). Such solutions should not, therefore, be treated without special directions from the instructor.[1]

2. If no precipitation occurs on the addition of HCl to a neutral or acid solution, $\overset{.}{Ag}$ and $\overset{..}{Hg}$ are absent. $\overset{.}{Pb}$ may, however, be present in small amounts and not be precipitated, as its chloride is soluble to the extent of 1 1/2% in cold water (see L. C., p. 341 (*c*); S. C., p. 457).

3. $HgCl_2$ is sufficiently soluble so that the mercuric ion, $\overset{..}{Hg}$, is not precipitated with this group.

4. If $\overset{..}{Bi}$ or $\overset{...}{Sb}$ are present, they may be precipitated in dense amorphous form as BiOCl or SbOCl. These substances, however, dissolve readily in a sufficient excess of HCl; hence the reason for adding this reagent to one-tenth the total volume of the solution. If the quantity of $\overset{..}{Bi}$ or $\overset{..}{Sb}$ is very great, additional acid may be required to effect complete solution.

5. In case the original solution is very concentrated, the addition of HCl may cause the precipitation of NaCl, $BaCl_2$, etc., in granular form. These, however, readily dissolve on the addition of water.

[1] In general any precipitate obtained by acidifying an alkaline solution with HCl must be gotten into solution again by means of the methods mentioned on p. 70 *et seq.*, and then subjected to the regular methods of analysis.

ANALYSIS OF THE SILVER GROUP.

1a. Wash the group precipitate on the filter-paper repeatedly with hot water.

Filtrate, $PbCl_2$.[1]

1b. Divide into two portions. To one portion add dilute H_2SO_4. A white precipitate, $PbSO_4$, soluble in NaOH, indicates the presence of lead.

To the other portion add K_2CrO_4 solution. A yellow precipitate, $PbCrO_4$, soluble in NaOH, indicates the presence of lead.

Residue, AgCl, HgCl.

1c. Measure out 5 c.c. NH_4OH and pour it over the residue collecting the filtrate in a test-tube. Pour this filtrate back over the residue, and so continue for several times.

Filtrate, $Ag(NH_3)_2Cl$.

1d. Confirm by acidifying with dilute HNO_3. A white precipitate, AgCl, indicates the presence of silver.

Residue, black.

Probably $Hg(NH_2)Cl + Hg$.
1e. Tear off that portion of the filter-paper covered with the most of the residue, place in a test-tube, and pour over it a few drops of aqua regia. Warm,[2] dilute, and filter until clear. Add a little $SnCl_2$ solution to the filtrate. A white precipitate, HgCl, or a gray one, Hg indicates the presence of mercury as Hg in the original solution.

[1] Also Pb̈ and Cl′. Usually in a group analysis the ions will not be indicated. However, when *many* substances are in solution only the ions with which we are concerned will be given.

[2] Whenever warming aqua regia or any strongly acid solution, the operation should be carried on under the hood.

NOTES ON THE ANALYSIS OF THE SILVER GROUP.

1. $PbCl_2$ dissolves rather slowly in hot water, and hence may not be completely removed by the treatment in 1*a*. In this case the first filtrate after adding NH_4OH[1] may be turbid on account of the formation of a basic salt of lead. This is, however, removed by subsequent filtration, and its presence in the residue does not interfere with the test for mercury.

2. The solubility of $PbSO_4$ and $PbCrO_4$ in NaOH distinguish these precipitates from the corresponding ones of barium which might be formed here in case the group precipitate was not sufficiently washed. These lead salts dissolve in NaOH on account of the amphoteric character of $Pb(OH)_2$. See p. 12.

3. Ammonia[1] forms with AgCl soluble $Ag(NH_3)_2Cl$, the ions of which are $Ag(NH_3)_2^\cdot$ and Cl'. In forming the complex ion $Ag(NH_3)_2^\cdot$ the concentration of the Ag is diminished below its value in a saturated solution of AgCl, and hence the AgCl dissolves. See principle 2, p. 8, and explanation on the page following.

4. In case the quantity of silver is very small, the AgCl may be more or less completely reduced by the Hg set free by the treatment with ammonia. Usually, however, if present, sufficient AgCl will dissolve so that silver is identified without difficulty. The reduced silver will be reconverted into AgCl during the identification of mercury and may be recognized as a slight curdy precipitate after the treatment with aqua regia. In this case it may be washed thoroughly and identified in the usual manner.

5. For the action of ammonia on the salts of mercury see L. C., p. 324, or S. C., p. 438.

[1] The student must form the habit of considering ammonia solution as containing the following substances: $NH_3, NH_4OH, NH_4^\cdot, OH'$, their concentrations diminishing in the order in which they are given, except that the two ions are present in equal concentration, which in a normal solution is about $0.004N$.

PRECIPITATION OF THE COPPER-TIN GROUP.

2–3(A). Warm the filtrate from the Silver group, dilute with 100–150 c.c. hot water, and pass H_2S through the solution for 10 to 15 minutes.[1] Filter.   In order to see whether precipitation has been complete dilute a small portion of the filtrate with an equal volume of hot water, and allow H_2S to run into it again. If a precipitate falls, dilute the whole filtrate and allow H_2S to run through in the same manner.   Filter, and repeat the above process with the filtrate until no further precipitate is obtained. Wash the precipitate with hot water until free from acid.

Precipitate:[2]	Filtrate:
HgS, PbS, CuS, CdS, Bi_2S_3, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2. Proceed to the separation of the Copper group from the Tin group.	Ions of the following groups: $\overset{..}{Fe}$, $\overset{..}{Al}$, etc. Boil at once until H_2S is expelled (Note 6). Proceed to the precipitation of the Iron group, p. 37 or 40.

[1] It is frequently an advantage to try only a very small portion of the solution with H_2S first.   If no precipitate is obtained, the group is absent and the tedious process of expelling H_2S from the major portion of the solution is obviated.

[2] Gold and platinum, if present in the solution, will be precipitated here and pass subsequently into the Tin group.

NOTES ON THE PRECIPITATION OF THE COPPER-TIN GROUP.

1. For a discussion of the different classes of metallic sulphides see L. C., p. 180; S. C., p. 254

A knowledge of the colors of the sulphides which may be precipitated here is important. These colors are: HgS, PbS, CuS, black; Bi_2S_3, SnS, dark brown; CdS, As_2S_3, As_2S_5, SnS_2, yellow; Sb_2S_3, Sb_2S_5, reddish or orange. For the reason for the appearance of PbS in this group, see p. 25, Note 2.

2. The solution is diluted to facilitate the precipitation of the sulphides. It accomplishes this, first, by diluting the acid added to precipitate the Silver group, and secondly, on account of the slight solubility of H_2S it furnishes more water in which this gas can dissolve, so that the chances of contact between it and the metallic ions are increased. This dilution may precipitate $BiOCl$ and $SbOCl$. This, however, does no harm, as these substances are readily changed into the sulphides by the action of H_2S.

3. Since H_2S is a reducing agent, the presence in the solution of any strong oxidizing agent oxidizes it to S (or H_2SO_4). Such substances are nitric acid, ferric salts, chromates, dichromates, and permanganates (see p. 14). Of course, these substances destroy the H_2S, and hence greatly retard the precipitation of the metallic sulphides. Nitric acid is the worst offender in this respect, and if present in any considerable quantity must be expelled by repeated evaporation to dryness with excess of HCl.

4. On first passing in H_2S various colored double salts of mercury and lead containing sulphur may be precipitated; for example $HgCl_2 2HgS$ is white, $PbCl_2 PbS$ is red. Excess of H_2S, however, converts all of these into the normal sulphides.

5. Most of these sulphides are precipitated more rapidly from a hot solution. This is notably true of the sulphides of arsenic; in fact, As_2S_5 is not appreciably precipitated from cold solutions and only very slowly from hot.[1] The presence of concentrated HCl also favors the precipitation. If, therefore, the presence of As is suspected, the solution should not be diluted at first, and H_2S should be passed through for an hour or more.

6. H_2S must be expelled from the filtrate, for otherwise when NH_4OH is added during the precipitation of the Iron group the Zinc group will be precipitated, at least, in part. Furthermore, if the filtrate is allowed to stand a long time the H_2S may be oxidized to H_2SO_4 and cause the precipitation of members of the Calcium group.

[1] Reduction goes on at the same time, so that the final precipitate consists of a mixture of As_2S_3 and As_2S_5.

SEPARATION OF THE COPPER GROUP FROM THE TIN GROUP.

2–3(B). Treat a small portion of the Copper-Tin group precipitate with 10 drops of yellow ammonium sulphide, dilute with an equal volume of water, and warm for a few minutes.

(*a*) If a residue remains undissolved, the Copper group is present.

(*b*) If the precipitate dissolves completely, the Tin group only is present.

In case result (*a*) is obtained, filter, and wash with hot water. Acidify this filtrate or the solution of (*b*) with dilute HCl (Note 4).

(*c*) A light colored (white or dirty white) precipitate is due to sulphur only.[1]

(*d*) A yellow or reddish colored precipitate indicates the presence of the Tin group (see Note 3). [Au_2S_3 or PtS_2,[2] if present, may give the precipitate a dark color.]

In case indications (*a*) and (*c*) only are obtained, analyze the remainder of the Copper-Tin group precipitate for the Copper group alone (p. 32).

In case indications (*b*) and (*d*) only are obtained, analyze the remainder of the Copper-Tin group precipitate for the Tin group alone (p. 34).

In case indications (*a*) and (*d*) are both obtained it is necessary to proceed with the separation of the Copper group from the Tin group, which is accomplished as follows:

Place the remainder of the Copper-Tin group precipitate in a large test-tube (1 in. diameter), add 5 to 20 c.c. yellow ammonium sulphide according to the volume of the precipitate and an equal volume of water, and let stand in a boiling water-bath 10 to 15 minutes with occasional shaking. Remove from the bath, boil for a moment over a free flame, filter, and wash with hot water.

2. Residue, Copper Group: HgS, PbS, CuS, CdS, Bi_2S_3. Analyze as directed on page 32.

Filtrate: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$. Acidify with dilute HCl, filter, wash with hot water, and dry by suction.

3. Precipitate, Tin group. As_2S_5, Sb_2S_5, SnS_2. Analyze as directed on page 34.[2]

Filtrate. Reject.

[1] Sulphur is obtained when yellow ammonium sulphide is decomposed by an acid, viz.: $(NH_4)_2S_x + 2HCl \longrightarrow 2NH_4Cl + H_2S + (x-1)S$.

[2] In case gold or platinum may be present, see Appendix, p. 84.

NOTES ON THE SEPARATION OF THE COPPER GROUP FROM THE TIN GROUP.

1. Yellow ammonium sulphide is ordinary ammonium sulphide, $(NH_4)_2S$, with sulphur dissolved in it (frequently written $(NH_4)_2S'_x$). All of the Tin group sulphides except SnS will dissolve in ordinary ammonium sulphide. SnS is oxidized by the extra sulphur in the yellow ammonium sulphide to SnS_2, after which it readily dissolves.

2. Soluble ammonium sulpho salts are formed with all of the Tin group sulphides by the action of yellow ammonium sulphide. For the reactions see S. C., pp. 455, 466, 469. Hydrochloric acid decomposes the sulpho salts, reprecipitating the sulphides in the higher state of oxidation (S. C., p. 466).

3. The sulphides of the Copper group are not acted upon by yellow ammonium sulphide, except CuS, which is partially dissolved. When, therefore, copper is present, the reprecipitated sulphides of the Tin group may have a liver-colored appearance due to the presence of some CuS. This does not, however, interfere seriously with the detection of the ions of the Tin group.

Na_2S_x is frequently used instead of $(NH_4)_2S_x$ to avoid this difficulty, but this reagent dissolves HgS, so unless mercury is absent this leads to other troubles.

4. Yellow ammonium sulphide is a strongly alkaline liquid. Litmus-paper must therefore always be used to make sure that sufficient HCl has been added before making any decision as to the color of the precipitate in (c) or (d), see opposite page.

ANALYSIS OF THE COPPER GROUP.

2a. Transfer the group precipitate to a casserole, add 10 to 15 c.c. dilute HNO_3, boil for two or three minutes, filter, and wash with hot water.

Residue, HgS.

2b. Transfer to a test-tube, dissolve in a few drops of hot aqua regia, dilute, and filter. To the clear filtrate add a few drops of $SnCl_2$. A white precipitate, HgCl, or a gray one, Hg, indicates the presence of mercury as $\overset{..}{Hg}$ in the original solution.

Filtrate, $Pb(NO_3)_2$, $Cu(NO_3)_2$, $Cd(NO_3)_2$, $Bi(NO_3)_3$.

2c. Evaporate almost to dryness on a water-bath, dissolve the residue in a small quantity of water (a few drops of HNO_3 may be used, if necessary to effect solution, Note 4), transfer to a test-tube, and add dilute H_2SO_4. Let stand for 10 minutes, shaking from time to time. A fine white precipitate, $PbSO_4$, indicates the presence of lead. Filter.

Filtrate, $\overset{..}{Cu}$, $\overset{..}{Cd}$, $\overset{...}{Bi}$, NO_3', SO_4''.

2d. Make alkaline with NH_4OH, stirring while adding the reagent. Filter, and wash with hot water.

Precipitate, $Bi(OH)_3$.

2e. Place a large beaker of water under the funnel, and then allow 3 or 4 drops of conc. HCl to fall upon the precipitate. A turbidity in the water, BiOCl (L. C., p. 224; S. C., p. 470), indicates the presence of bismuth.

Filtrate, $Cu(NH_3)_4''$, $Cd(NH_3)_4''$, NO_3', SO_4''.

2f. If the filtrate is blue, copper is indicated. Test for cadmium according to *2g.*

If the filtrate is not blue, test for copper as follows:

Acidify with acetic acid, and divide into two portions. To one portion add a few drops of $K_4Fe(CN)_6$ solution. A mahogany-colored precipitate, $Cu_2Fe(CN)_6$, indicates the presence of copper. Test for cadmium as in *2h.*

2g. Add to three-fourths of the blue filtrate KCN solution until the blue color disappears, and then pass H_2S through it. A yellow precipitate, CdS, indicates the presence of cadmium.

2h. Pass H_2S directly through the second portion of the solution of *2f.* A yellow precipitate, CdS, indicates the presence of cadmium.

NOTES ON THE ANALYSIS OF THE COPPER GROUP.

1. The action of HNO_3 upon the sulphides which it dissolves is primarily one of oxidation and not of double decomposition (S. C., pp. 298–9).

2. HgS is frequently converted into white insoluble $Hg(NO_3)_2\cdot 2HgS$ by HNO_3. Hence any residue regardless of color (except a floating mass of free sulphur) should be tested for mercury.

3. Some PbS may be oxidized to insoluble $PbSO_4$ by the HNO_3 and so remain with the residue. In case conc. HNO_3 is not employed, however, the quantity so oxidized is not sufficient to affect the identification of lead.

4. $PbSO_4$ is more soluble in HNO_3 than in water, hence the reason for expelling the excess of this acid by evaporation before making the test for lead. Since but little Pb can occur here anyway (see p. 25, Note 2) considerable care should be exercised in making this test. If a residue remains after the evaporation which is difficult to dissolve, it should be filtered out, and, in case no bismuth is found later, it should be tested for bismuth exactly as in 2e.

5. Copper and cadmium are precipitated as hydroxides on neutralizing with NH_4OH, but form soluble complex ions with excess of the reagent (see L. C., p. 294; S. C., p. 414). Even in the absence of bismuth a small precipitate is frequently obtained at this point on account either of the insufficient washing of the group precipitate or of the imperfect separation of the Tin group.

6. The test for copper with $K_4Fe(CN)_6$ is more delicate than the blue color with NH_4OH. Cd gives a white precipitate with this reagent. Cü is, however, usually absent if no blue color is obtained when NH_4OH is added.

7. With KCN copper and cadmium form complex ions, $Cu(CN)_2'$ and $Cd(CN)_4''$, of which the former is much more stable, yielding but very few Cu ions while the latter yields more Cd ions (see L. C., pp. 298 and 322; S. C., p. 415). Introducing the S'' therefore precipitates CdS but not Cu_2S. (For the principle involved see pp. 7–8.) Cü is reduced to Cu by KCN.

8. In case the precipitate of 2g or 2h is black, some of the previous separations have been imperfect. Treat such a precipitate in the following manner: Transfer to a test-tube and boil with $2N$ H_2SO_4 for a few minutes, filter, dilute the filtrate with considerable water, and pass in H_2S. A yellow precipitate indicates the presence of cadmium.

ANALYSIS OF THE TIN GROUP.

3*a*. Treat the group precipitate, which should be as dry as possible, with 5 to 10 c.c. $12.9N$ HCl (must be measured in a graduate), place in boiling water bath, and allow it to remain there with frequent shaking for about 10 minutes. Filter, and wash with 3 c.c. $8N$ HCl, allowing it to run into the filtrate, then wash with hot water.

Residue, As_2S_5.

3*b*. Dissolve in 2 to 3 c.c. of hot conc. HNO_3, evaporate most of the excess of acid, dilute to about 5 c.c., and filter. Divide into two portions.

To one portion add $AgNO_3$ solution, filter, if a precipitate forms, and add more $AgNO_3$ to make sure no further precipitation occurs. Neutralize carefully with very dilute NH_4OH. A brick-red precipitate, Ag_3AsO_4, indicates the presence of arsenic. Add the second portion to 5 c.c. ammonium molybdate solution, warm to 40°, and let stand 2 to 3 hours. A yellow precipitate indicates the presence of arsenic.

Filtrate, $SbCl_3$, $SnCl_4$.[1]

3*c*. Dilute with 8 c.c. water plus three times as much water as the volume of $12.9N$ HCl employed in the first case above, heat to 90°, place in a hot water bath, and pass in H_2S for a few minutes. If a reddish precipitate forms, antimony is indicated. Filter. Dilute the filtrate with 5 c.c. water, heat to 90°, and repeat the addition of H_2S as before, provided that the reddish precipitate continues to form. (If the precipitate which forms here is very dark brown or yellow,[2] proceed as under 3*e*, next page.)

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[1] The following method of separation of antimony and tin is essentially that of Noyes and Bray, *Journ. Am. Chem. Soc.*, 29, pp. 180–1, (1907).

[2] A brown precipitate is probably stannous sulphide and a yellow one stannic sulphide.

(From 3c)

Precipitate, Sb_2S_3. ·

Filtrate, $SnCl_4$.

3d. If the precipitate is dark colored, antimony must be confirmed as follows: Dissolve in very little $8N$ HCl, boil to remove H_2S, and then pour over a piece of tin on a platinum foil. A black spot on the platinum, insoluble in NaClO, indicates the presence of antimony.

3e. Dilute with half the volume of water thus far added, cool, and pass in H_2S. If a precipitate does not form, tin is absent. If a yellowish or brownish precipitate begins to fall transfer at once to a porcelain dish without filtering, and evaporate to 5 to 10 c.c. (the liquid should now be clear). Place in it a piece of pure zinc, and allow the action to proceed until most of the zinc has dissolved. Rub the zinc to dislodge particles of tin, remove the zinc as completely as possible, and wash the particles of tin several times by decantation. Dissolve them in hot $8N$ HCl, filter clear, and add $HgCl_2$ solution to the filtrate. A white precipitate, HgCl, or a gray one, Hg, indicates the presence of tin.

NOTES ON THE ANALYSIS OF THE TIN GROUP.

1. Sb_2S_5 dissolves but slowly in HCl, so that the action must be continued for some time. Reduction takes place simultaneously, so that $SbCl_3$ results. Boiling must be avoided, as this evaporates HCl rapidly, and the acid soon becomes too dilute. Some As_2S_5 may dissolve during this process, in which case it will appear later in the test for antimony. Arsenic is, however, distinguished from antimony by being readily soluble in NaClO.

2. Boiling with HNO_3 oxidizes As_2S_5 to H_3AsO_4.

3. Ag_3AsO_4 is soluble both in acids and in ammonia, hence it will not be precipitated except in a rigorously neutral solution. This is frequently most easy to accomplish by allowing dilute

NH_4OH to run down on to the top of the solution and seeing whether or not a precipitate forms at the neutral layer.

4. Arsenic acid forms with ammonium molybdate a compound known as ammonium arseno-molybdate, similar in composition to ammonium phospho-molybdate (see p. 63).

5. The separation of antimony from tin depends upon the insolubility of Sb_2S_3 in *hot* $2.3N$ (8%) HCl and the solubility of SnS_2 under the same conditions.   If much HCl has been allowed to evaporate during the separation of arsenic in 3a, it causes, of course, considerable uncertainty in attaining the proper concentration of acid for this separation.   Allowance has been made for a certain amount of evaporation of HCl in the directions for diluting given in 3c.

6. For the nature of the test for tin see p. 23, Note 7.

INTERFERING SUBSTANCES.[1]

[In case the optional method for the precipitation and analysis of the Iron-Zinc group is employed, omit this; but see p. 82.]

In case the original solution was prepared from a solid substance by means of acids (p. 70) certain anions may be present which cause serious complications in the separation and analysis of the groups which follow, provided they are not removed at this point. Such anions are PO_4''', C_2O_4'' (and F').[2] Furthermore, silicic acid and organic matter, if present, may also cause trouble at this point. If, however, directions were accurately followed at the time of making the solution, these last-mentioned substances will have been removed (see Notes 1 and 2, p. 71). Since the tests for anions are not usually made until after the basic analysis has been completed, it is necessary before proceeding to test for PO_4''' and C_2O_4'' in the filtrate from the Copper-Tin group, provided NH_4OH gives a precipitate with a small portion of it.

Test for PO_4'''.—To a small portion of the filtrate from the Copper-Tin group, free from H_2S, add HNO_3, and then add this solution drop by drop to 5 c.c. ammonium molybdate solution warmed to 40°. If no precipitate appears at once, let stand for some time. A yellow precipitate indicates the presence of PO_4''' (see test 1, p. 63).

Removal of PO_4'''.—This is effected by means of $\overset{\cdots}{Fe}$ in the precipitation of the Iron group (see Note 6, p. 41).

Test for C_2O_4''.—A small portion of the filtrate from the Copper-Tin group is added drop by drop to 10 c.c. of hot $2N$ Na_2CO_3. Allow to stand a few minutes with occasional warming and shaking. Filter, acidify the filtrate with acetic acid, and add a few drops of $CaCl_2$ solution. A white precipitate, CaC_2O_4, indicates C_2O_4''.

Removal of C_2O_4''.—This is accomplished in a manner very similar to the test just given. About 50 c.c. $2N$ Na_2CO_3 is placed in an Erlenmeyer flask, heated to boiling, and all the filtrate from the Copper-Tin group added in small portions at a time (a few grains of Na_2O_2 are also added to oxidize $\overset{\cdots}{Fe}$ to $\overset{\cdots}{Fe}$ and $\overset{\cdots}{Mn}$

[1] This is to be omitted by the student unless the substance submitted for analysis is a solid having the properties described in the first sentence.

[2] Occurs very rarely. It is removed in the same manner as C_2O_4''.

to $\overset{...}{Mn}$). After 5 minutes cool, filter, and wash thoroughly with hot water.

A. Precipitate:

$Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, $Mn(OH)_3$, $ZnCO_3$, $NiCO_3$, $CoCO_3$, $CaCO_3$, $SrCO_3$, $BaCO_3$, $MgCO_3$.

Dissolve in dilute HCl, and proceed to the precipitation of the Iron group, etc.

B. Filtrate:

C_2O_4'', $\overset{.}{Na}$, $\overset{.}{Li}$, $\overset{.}{K}$, $\overset{.}{NH_4}$, and possibly AlO_3''', CrO_3''', or CrO_4'',

If aluminium and chromium are not found in the Iron group, they must be tested for in this filtrate as follows:

Chromium.—Boil a small portion of the filtrate with Na_2O_2 for a few minutes, filter, and acidify with H_2SO_4. A blue color, $HCrO_5$, indicates the presence of chromium.

Aluminium.—Acidify another portion with HCl, boil to expel CO_2, and make just alkaline with NH_4OH. If the precipitate is white, aluminium is indicated. If it is greenish, some $\overset{...}{Cr}$ is present. In this case boil the precipitate with KOH, filter, and test the filtrate again with HCl and NH_4OH for aluminium.

The rest of the filtrate is tested for $\overset{.}{K}$ and $\overset{.}{Li}$ as directed on p. 50.

NOTES ON INTERFERING SUBSTANCES.

1. The phosphates and oxalates of the heavy metals are insoluble in neutral or alkaline solution or in solutions acid with weak acids, as acetic. Hence, when PO_4''' or C_2O_4'' is present, phosphates of the metals of the Zinc and Calcium groups may be precipitated with the Iron group. For the same reason it is useless to test for PO_4''' and C_2O_4'' at this point, if the original substance was a solid soluble in water.

2. Organic matter may entirely prevent the precipitation of the Iron group. If present, however, it should be detected in the closed-tube test (p. 66), and removed before preparing the solution. In removing organic matter oxalic acid is destroyed, and hence it is useless to test for oxalates in such a case.

3. Aluminium and chromium compounds on treatment with strong alkalies are apt to be converted into aluminates and chromites (or chromates in case too much Na_2O_2 is used) and will therefore be found in the filtrate after the treatment with Na_2CO_3. At the high temperature employed, however, chromites are usually decomposed, so that chromium is seldom found in this filtrate, except in cases where too much Na_2O_2 is used.

4. Large excess of Na_2CO_3 is of course present in the filtrate. This interferes with the flame test for lithium. The test for this element must therefore be made with the spectroscope. The presence or absence of ammonium and sodium has already been determined in the preliminary tests (p. 22).
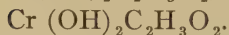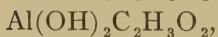
PRECIPITATION OF THE IRON GROUP.

[For optional method for the precipitation and analysis of this and the next groups, see p. 80.]

4. If the preliminary tests have shown the presence of iron, the filtrate from the Copper-Tin group, from which H_2S has been expelled, is boiled with 2 to 3 c.c. $8N$ HNO_3 to oxidize $\overset{..}{Fe}$ to $\overset{...}{Fe}$. To this solution, or to the filtrate from the Copper-Tin group in case iron is absent, are added 5 c.c. NH_4Cl^1 and then NH_4OH very carefully until just alkaline, or until a precipitate begins to form. If no precipitate forms on neutralizing, the Iron group is absent, and one should proceed at once to the separation of the Zinc group.[2]

If a precipitate does begin to form on adding NH_4OH, it should be of a brown or reddish color. If not, dissolve it in the least quantity of dilute HCl, add 5 c.c. $FeCl_3$, and just neutralize again. Repeat this process, if necessary, until the precipitate which falls has the right color. Just dissolve this last precipitate in HCl, add 10 to 15 c.c. $4N$ $NH_4C_2H_3O_2$, dilute to 500 c.c. with hot water, and boil for a few minutes.[3] Keep hot while filtering, and wash with boiling water until free from acid.
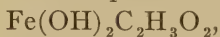
Precipitate:	Filtrate:
$Fe(OH)_2C_2H_3O_2,$	Ions of the following groups:
$Al(OH)_2C_2H_3O_2,$	$\overset{..}{Ni}$, $\overset{..}{Zn}$, etc. Boil down to 100
$Cr(OH)_2C_2H_3O_2.$	c.c. and proceed to the precipi-

Analyze according to direction tation of the Zinc group, p. 43. on p. 42.

[1] In case HCl was added to the solution to precipitate the Silver group, sufficient NH_4Cl will be formed on neutralizing with NH_4OH.

[2] If none of the interfering substances, p. 37, are present, the elementary student may be more successful in precipitating this group as follows: Continue adding NH_4OH to slight excess, boil, filter, and wash some with hot water. Redissolve the precipitate in dilute HCl, dilute to 50 c.c., add NH_4Cl and NH_4OH to slight excess, boil, filter, and wash free from alkali with hot water. Combine the two filtrates and use for the precipitation of the Zinc group, p. 43. The precipitate may contain $Fe(OH)_3$, $Cr(OH)_3$, $Al(OH)_3$, and perhaps some $Mn(OH)_3$ (see Note 7).

[3] Students are very apt to have the solution too acid at this point, which prevents complete precipitation. A few drops of NH_4OH may therefore be added, *but not enough to neutralize the acid completely*. A small portion of the filtrate should be boiled with excess of HNO_3 and tested with $K_4Fe(CN)_6$ to make sure that it is free from iron.

NOTES ON THE PRECIPITATION OF THE IRON GROUP.

1. The fact that a precipitate is obtained with NH_4OH does not necessarily indicate that this group is present. Such a precipitate may be due to manganic hydroxide or to the phosphates or oxalates of the metals of the groups following (read pp. 37–39).

2. The presence of NH_4Cl prevents the precipitation of the hydroxides of some of the metals of the groups following, notably magnesium (see p. 9, also L. C., p. 121; S. C., p. 429).

3. The precipitation of the basic acetates is a hydrolytic action (see p. 11, also L. C., p. 144), for which a high temperature is required. The action being reversible it is necessary to keep the solution hot while filtering. The formulas given for the precipitate are probably not the true ones. They will answer for the writing of equations. For a discussion of the probable formulas, see Weinland and Gussmann, Zeitsch. anorg. Chem., 66, 162, (1910).

4. The acetates of the bivalent cations are not sufficiently hydrolyzed to be precipitated, hence $\overset{..}{Fe}$ must be oxidized to $\overset{...}{Fe}$ (see p. 14). Any $\overset{..}{Fe}$ remaining unoxidized will be precipitated with the next group, and is apt to lead to confusion in the analysis.

5. Chromium as chromate or dichromate is not precipitated here. These substances are, however, reduced by H_2S. Hence, if this reagent was passed through the solution for a sufficient length of time in precipitating the Copper-Tin group, all of the chromium will be in the form of $\overset{...}{Cr}$. This last ion is precipitated as basic acetate only in the presence of ferric acetate. For this reason it is necessary to add $\overset{...}{Fe}$ (as $FeCl_3$), if it is not already present in sufficient amount. One judges of this by the color of the precipitate, as $\overset{...}{Fe}$ is the only one of the ions of this group which gives a brown or reddish precipitate with NH_4OH.

6. In case $\overset{...}{PO_4}''$ is present, excess of $\overset{...}{Fe}$ effects its removal as $FePO_4$ without precipitating the phosphates of the metals of the Zinc or Calcium groups.

7. If the method of footnote 2, opposite page, is used for the precipitation of this group, $\overset{..}{Mn}$, $\overset{..}{Zn}$ and $\overset{..}{Co}$ may be carried down to a certain extent by the hydroxides of iron, aluminium and chromium. Reprecipitation gets rid of the $\overset{..}{Zn}$ and $\overset{..}{Co}$, and that portion of the $\overset{..}{Mn}$ which has not been oxidized to $\overset{...}{Mn}$. Usually sufficient manganese will be left in the solution so that it can be readily identified in the Zinc group. If, however, it is suspected that it has all been precipitated with the Iron group, it may be tested for by fusing some of the Iron group precipitate as in 5g, p. 45.

ANALYSIS OF THE IRON GROUP.

The presence of iron has already been determined in the preliminary tests. Divide the group precipitate into two portions.

4a. In a test-tube mix one portion of the precipitate with a little water, add a small quantity Na_2O_2, shake for a few minutes, and filter.

Residue, reject.	Filtrate, Na_2CrO_4.

4b. Make acid with acetic acid. A transient blue color, due to $HCrO_5$[1] (report at once), indicates the presence of chromium.

As a second test evaporate the solution to dryness, extract the residue with hot water, make acid with acetic acid (if not already so), and add a little $Pb(C_2H_3O_2)_2$ solution. A yellow precipitate, $PbCrO_4$, indicates the presence of chromium.

4c. To the second portion of the group precipitate add 10 c.c. NaOH,[2] boil for a few minutes (look out for bumping), and filter.

Residue, reject.	Filtrate, Na_3AlO_3.

4d. Acidify with dilute HCl, make just alkaline with NH_4OH, and heat to boiling. A white gelatinous precipitate, $Al(OH)_3$, indicates the presence of aluminium. It should be confirmed as follows: Filter, dry the precipitate on a platinum foil, moisten with a drop of $Co(NO_3)_2$ solution, and then heat to a high temperature over the Bunsen burner. A blue residue, $Co(AlO_2)_2$, indicates the presence of aluminium.

NOTES ON THE ANALYSIS OF THE IRON GROUP.

1. Na_2O_2 oxidizes the basic chromium acetate to Na_2CrO_4 which is soluble (see p. 14).

2. In connection with the first test of 4b, consult L. C., p. 346. In the second test evaporation to dryness is necessary to destroy the peroxide. Acetic acid is added because $PbCrO_4$ is soluble in an alkaline solution.

3. For the action of NaOH upon the compounds of aluminium, see p. 12, also L. C., p. 329 (c) or S.C., pp. 444–5. Although cold NaOH has a similar action upon chromium compounds, boiling finally causes the formation of insoluble $Cr(OH)_3$.

[1] See Riesenfeld, *Berichte*, 41, 2826.

[2] The NaOH solution should be pure and freshly prepared, as otherwise it may contain silicates dissolved from the glass. Silicates are decomposed by HCl with separation of gelatinous silicic acid, H_2SiO_3, which very much resembles $Al(OH)_3$. Pure NaOH may be prepared by the double decomposition of Na_2CO_3 and $Ba(OH)_2$ These two substances may be mixed in the first place with the precipitate to be treated, 10 c.c. water added, and the process then carried out exactly as above.

PRECIPITATION OF THE ZINC GROUP.

5. Make the filtrate from the Iron group which has been boiled down to a volume of 100 c.c.[1] just alkaline with NH_4OH. Heat to boiling, add 5–10 c.c.[2] $(NH_4)_2S$, filter at once, and wash with hot water containing a little H_2S and NH_4Cl until free from alkali.

Precipitate:	Filtrate:
NiS, CoS, ZnS, MnS. Analyze according to directions on next page.	Ions of the following groups: Ca̤, Ba̤, etc. Proceed to the separation of the Calcium group, p. 46.

NOTES ON THE PRECIPITATION OF THE ZINC GROUP.

1. NiS tends to form a colloidal solution, or perhaps a soluble double ammonium sulphide, in which case the filtrate is colored black. This is best prevented by avoiding too great alkalinity; hence the least possible amounts of NH_4OH and $(NH_4)_2S$ should be employed. If, however, the filtrate is black, make it just barely acid with acetic acid, boil, and filter through a clean paper.

2. The NH_4Cl in the wash-water tends to prevent the formation of colloidal solutions of the sulphides while washing. All of these sulphides are readily oxidized to sulphates by the oxygen of the air. The H_2S in the wash-water is to prevent this. After washing, the separation of cobalt and nickel from manganese and zinc must be undertaken at once to prevent further oxidation.

3. These sulphides have the following colors: CoS and NiS, black; MnS, light pink; ZnS, white. For the difference in behavior of these sulphides and those of the Copper-Tin group, consult the reference, Note 1, p. 29.

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[1] NH_4Cl must be added here in case it is not already present.

[2] More may be needed in some cases. Always test the filtrate with more of the reagent.

ANALYSIS OF THE ZINC GROUP.

5a. Treat the group precipitate with cold dilute HCl, stir for a few minutes, filter, and wash with water containing H_2S.

Residue, black, CoS, NiS.   Filtrate, see below.

5b. Make a borax bead test (p. 69) with a little of the residue.

A blue bead indicates cobalt.

A brown or grayish-brown bead indicates nickel.

In either case dissolve the remainder of the residue in a little hot aqua regia, dilute, filter. (Reject any residue.)

5c. In case a brown bead was obtained above cobalt is probably absent, and nickel is confirmed by making this filtrate alkaline with Na_2CO_3 solution and boiling. A pale green precipitate, $Ni_2(OH)_2CO_3$, indicates the presence of nickel.

5d. In case cobalt was indicated in the bead test, nickel may also be present, and it is then necessary to separate these elements, which is accomplished in the following manner (see Note 1):

Evaporate just to dryness in a porcelain dish (not to oxide), add a few drops of dilute HCl and about 10 c.c. hot water. Transfer to a test-tube, and add a solution of nitroso-beta-naphthol in slight excess, shake well, allow to stand for a few minutes, and filter.

Precipitate, brick red $Co(C_{10}H_6ONO)_3$ indicates cobalt.   Filtrate may contain Ni. Test again with nitroso-beta-naphthol to remove any remaining Co.

5e. To the filtrate add 6 c.c. dilute H_2SO_4 and 3 c.c. conc. HNO_3, and evaporate under the hood until fumes of SO_3 appear. (All organic matter should now be destroyed and the color of the solution be light yellow; if darker, repeat the treatment with acids.) Cool, cautiously add 5 c.c. water, put in a piece of litmus paper and make just alkaline with NH_4OH. Transfer to a test-tube and run in H_2S. A black precipitate is probably NiS. Confirm the presence of nickel by testing with the borax bead.

(From 5a).

Filtrate, $ZnCl_2$, $MnCl_2$.

5f. Boil to remove H_2S, make alkaline with NaOH, shake thoroughly, filter.

Precipitate, light colored, rapidly changing to brown, $Mn(OH)_2$.[1]

5g. Fuse some of the precipitate in the loop of a platinum wire with a mixture of Na_2CO_3 and KNO_3. A *dark* green[2] mass, Na_2MnO_4 (report at once), indicates the presence of manganese.

Filtrate, Na_2ZnO_2.

5h. Acidify slightly with acetic acid, and pass in H_2S. A white precipitate, ZnS, indicates the presence of zinc.

Confirm by drying on platinum, adding a drop of $Co(NO_3)_2$, and heating to a high temperature. Green $CoZnO_2$ confirms the presence of zinc.

NOTES ON THE ANALYSIS OF THE ZINC GROUP.

1. The method given for the separation of cobalt from nickel follows the procedure recommended by Chapin (Jour. Am. Chem. Soc., 29, 1029, 1907). For the method of preparing the solution see appendix.

In case nitroso-beta-naphthol is not kept in stock the following method depending on the insolubility of $K_3Co(NO_2)_6$ in acetic acid solution may be employed. Neutralize the filtrate from 5b with sodium carbonate, make strongly acid with acetic acid and add solid KNO_2 in excess, shaking from time to time until the latter dissolves. Let stand for an hour or two. A yellow precipitate indicates cobalt.

Filter, to the filtrate add NaOH until alkaline, and then boil. A light green precipitate indicates nickel, which should be confirmed by the borax bead test.

2. For the action of NaOH upon the compounds of zinc, see p. 12, also L. C., p. 319; S. C., p. 432. Manganese compounds are not thus affected, the hydroxide being simply precipitated.

3. For the oxidation of the lower compounds of manganese by means of Na_2CO_3 and KNO_3, see L. C., p. 352; S. C., p. 490.

4. Although ZnS can be precipitated from an alkaline solution, it is less apt to be contaminated with other substances when the solution is acid with acetic acid.

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[1] A precipitate is almost always obtained here even in the absence of manganese, due usually to either cobalt, nickel or iron. Unless, therefore, the precipitate behaves in the manner indicated, it is not worth while to make the test for manganese.

[2] If nickel is present here, a light green mass is obtained even in the absence of manganese.

PRECIPITATION OF THE CALCIUM GROUP.

6. Heat the filtrate from the Zinc group to boiling, and if any turbidity results, filter until clear.[1] Add $(NH_4)_2CO_3$ solution little by little to this hot solution as long as a precipitate continues to fall, heat gently for a few minutes, filter and wash with hot water until free from alkali.

Precipitate:	Filtrate:
$CaCO_3$, $SrCO_3$, $BaCO_3$.	$\overset{..}{Mg}$, $\overset{.}{Na}$, $\overset{..}{K}$, $\overset{.}{Li}$, $\overset{.}{NH_4}$.
Analyze according to the directions on p. 48.	Traces of $\overset{.}{Ca}$, $\overset{.}{Sr}$, or $\overset{.}{Ba}$ may still be present, which are detected in the following manner:[2] (a) To a small portion of the filtrate add a few drops of $(NH_4)_2SO_4$ solution, shake thoroughly, and observe whether any turbidity results. (b) To another small portion of the filtrate add a few drops of $(NH_4)_2C_2O_4$ solution, shake thoroughly, and see whether any turbidity results in this case.

If no turbidity results in either (a) or (b), reject these portions tested, and proceed to precipitate $\overset{..}{Mg}$ from the remainder of the filtrate (p. 50).

If turbidity does result in either one or in both of the tests, add the reagent or reagents which produced the turbidity to the remainder of the filtrate, shake, and filter.

Precipitate:	Filtrate:
$BaSO_4$, $(SrSO_4)$, CaC_2O_4.	$\overset{..}{Mg}$, $\overset{.}{Na}$, $\overset{.}{K}$, $\overset{.}{Li}$, $\overset{.}{NH_4}$.
Reject.	Proceed according to directions on p. 50.

[1] NH_4Cl must be added here if it is not already present.

[2] These tests should be made even when no precipitate has been obtained with $(NH_4)_2CO_3$, as this reagent may fail to show small quantities of $\overset{..}{Ba}$, $\overset{.}{Sr}$, or $\overset{..}{Ca}$ in the presence of large quantities of ammonium salts.

NOTES ON THE PRECIPITATION OF THE CALCIUM GROUP.

1. If difficulty is experienced in trying to remove any turbidity (probably due to traces of sulphur from oxidation of $(NH_4)_2S$) from the filtrate from the Zinc group, acidify it first with HCl, then boil, and filter. Finally make alkaline with NH_4OH and proceed with the precipitation of the Calcium group.

2. Boiling changes any soluble acid carbonates into the insoluble normal carbonates, thus:

$$H_2Ca(CO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2 \uparrow .$$

Too long boiling should, however, be avoided, as the reaction causing the precipitation may be reversed on account of the gradual decomposition of $(NH_4)_2CO_3$, thus:

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 \uparrow + H_2O + CO_2 \uparrow .$$
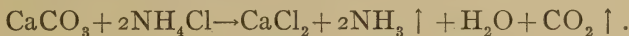
3. Magnesium is not precipitated here on account of the presence of NH_4Cl. The reasons for this are the same as those given for the non-formation of magnesium hydroxide on making alkaline with NH_4OH (consult reference, Note 2, p. 41).

ANALYSIS OF THE CALCIUM GROUP.

6a. Transfer the group precipitate to a casserole, add 10 c.c. acetic acid, and warm until the precipitate dissolves. Filter to remove particles of filter-paper, etc.

Test a small portion of the solution with $K_2Cr_2O_7$. If a precipitate forms,[1] add this reagent to the rest of the solution, shake thoroughly, and filter.

Precipitate, $BaCrO_4$.	Filtrate, $\overset{..}{Ca}$, $\overset{..}{Sr}$, $C_2H_3O_2'$, CrO_4''.
6b. Confirm by dissolving in dilute HCl and adding to the solution an equal volume of saturated $CaSO_4$. A white precipitate, $BaSO_4$, indicates the presence of barium.	6c. Remove the excess of chromate by reprecipitating with $(NH_4)_2CO_3$ solution, warming, filtering, and washing the precipitate. Reject the filtrate.

6d. Dissolve the precipitate in a few drops of dilute HNO_3, and evaporate nearly to dryness. Transfer to a test-tube, and add 8 to 10 c.c. amyl alcohol. Insert a thermometer, and boil (care!) until the temperature rises to 130°. (Add more amyl alcohol, if necessary, so that the total volume will not fall below 5 c.c.) Decant the liquid through a small dry filter-paper.

Residue, $Sr(NO_3)_2$.	Filtrate, $Ca(NO_3)_2$.
6e. Rinse the residue adhering to the test-tube with a little absolute alcohol, and decant through the filter-paper just used into the $Ca(NO_3)_2$ solution. Test any residue remaining for strontium with the spectroscope.	6f. Dilute with an equal volume of ordinary ethyl alcohol, and add dilute H_2SO_4. A white flocculent precipitate, $CaSO_4$, indicates the presence of calcium.

[1] If a precipitate does not form, proceed as follows: Add 2 to 4 c.c. conc. HNO_3 to the acetic acid solution, and evaporate to dryness. Then add three or four drops more of HNO_3, and evaporate again. Finally moisten with one drop HNO_3, and then proceed according to 6d: "Transfer to a test-tube, and add 8 to 10 c.c. amyl alcohol," etc.

NOTES ON THE ANALYSIS OF THE CALCIUM GROUP.

1. $K_2Cr_2O_7$ should not be added, if barium is absent, for this reagent has to be removed by reprecipitation of the carbonates before calcium and strontium can be separated. Hence the reason for testing only a small portion of the solution first with $K_2Cr_2O_7$.

2. $K_2Cr_2O_7$ solution contains enough CrO_4'' ions to cause the precipitation of $BaCrO_4$, provided Ba is present, but not enough to cause the precipitation of either $SrCrO_4$ or $CaCrO_4$. K_2CrO_4 solution contains many more CrO_4'' ions and would therefore cause the precipitation of the latter substances, provided much Sr or Ca were present. For the principles involved see p. 8.

3. Commercial amyl alcohol always contains water, and, since $Sr(NO_3)_2$ is insoluble only in the anhydrous liquid, it is necessary to expel the water by boiling. The completion of the dehydrating process is most conveniently indicated by means of a thermometer, as when the water is expelled the temperature rises to 130°, the boiling point of the anhydrous alcohol.

4. Small quantities of $Ca(NO_3)_2$ may remain undissolved mixed with the $Sr(NO_3)_2$. By means of the spectroscope, however, strontium is easily identified even in the presence of some calcium. A flame test made with care will suffice, if a spectroscope is not at hand.

5. Amyl alcohol does not mix with water in all proportions. Hence the filtrate is diluted with ordinary alcohol, in which both amyl alcohol and water are soluble, so that the homogeneous state may be preserved when $CaSO_4$ is precipitated.

6. The separation with amyl alcohol should be carried on under the hood. In case this reagent is not kept in stock or suitable hoods are not available the following method may be used, which is, however, not quite so delicate as the one given in the text, 6d. Dissolve the precipitate in acetic acid and test for strontium with the flame test and by means of the spectroscope. If it is present, add $(NH_4)_2SO_4$ solution, shake thoroughly, warm, let stand several minutes and then filter.

Precipitate, $SrSO_4$.   Filtrate may contain Ca.

6f. To the filtrate, or to the solution containing no strontium, add a little more acetic acid and then $(NH_4)_2C_2O_4$ solution. A fine white precipitate, CaC_2O_4, indicates the presence of calcium.

4

MAGNESIUM AND THE POTASSIUM GROUP.

7. To one-half the filtrate from the Calcium group[1] add Na_2HPO_4 solution. A white precipitate, $MgNH_4PO_4$, shows the probable presence of magnesium.[2]

Confirm as follows: Filter but do not wash the precipitate. Dissolve it by pouring a little dilute HCl over the filter-paper. Add NH_4Cl and then neutralize by adding NH_4OH drop by drop. The reappearance of the white precipitate in crystalline form confirms the presence of magnesium.

8. Evaporate the other half of the filtrate from the Calcium group to dryness in a porcelain dish, and continue to heat carefully over the free flame of the Bunsen burner until ammonium salts have been expelled (do not heat the bottom of the dish to redness). Collect together the residue at the bottom of the dish and moisten with dilute HCl.

Dip a clean platinum wire[3] into this residue and hold it in the Bunsen flame. A red color imparted to the flame indicates lithium; a violet color indicates potassium.

If much sodium is present, the test for lithium must be made with the spectroscope. If any sodium is present, view the flame through a piece of blue glass, or through a potassioscope (yellow light is thereby absorbed). The violet-colored flame of potassium, if it is present, can then be distinctly seen.

[1] If this solution does not contain NH_4Cl and NH_4OH (alkaline reaction), add these reagents to the portion to be tested for magnesium. If the filtrate is bulky, it should be boiled down to at least 50 c.c. before dividing into two portions.

[2] If a precipitate does not appear at once, allow to stand several hours, also stir the solution from time to time with a glass rod so as to scratch the inside of the test-tube.

[3] To clean the platinum wire, dip it into commercial HCl and then hold it in the Bunsen flame. Continue dipping it in the acid and holding it in the flame alternately until no color is imparted to the flame.

NOTES ON MAGNESIUM AND THE POTASSIUM GROUP.

1. All other cations except those of arsenic, antimony, and the alkali metals are precipitated by Na_2HPO_4, so that, unless these have been entirely removed, the test for magnesium is valueless. Hence the rigorous treatment to assure the absence of $\overset{\cdot}{Ca}$, $\overset{\cdot}{Sr}$, and $\overset{\cdot\cdot}{Ba}$ from the filtrate, p. 46.

2. $MgNH_4PO_4$ is a crystalline precipitate and forms but slowly from solutions which are only slightly supersaturated. Hence the treatment recommended in footnote 2, opposite page.

3. Only half of the filtrate is tested for magnesium, so as to avoid the presence of sodium in excess (from the Na_2HPO_4) in the residue which is to be tested for potassium and lithium.

4. No entirely satisfactory precipitants for $\overset{\cdot}{K},^1$ $\overset{\cdot}{Na}$ and $\overset{\cdot}{Li}$ are known. Hence recourse must be had to the flame and spectroscope tests for identifying these substances. The test for sodium has already been made among the preliminary tests.

5. Ammonium salts, having been added as group reagents in many cases, are present in the final filtrate in large quantities. Their removal renders the flame tests much more distinct. KCl is volatile at a red heat. Care must therefore be exercised not to let the dish become too hot when expelling ammonium salts.

6. Magnesium in the amount in which it is apt to be present here does not interfere with the flame tests for potassium and lithium, so that it is unnecessary to consume time in removing it. If present in large quantity, however, it may be removed as follows: Add $Ba(OH)_2$ solution until alkaline, and filter. Make the filtrate acid with dilute H_2SO_4. Keep warm for some time, then filter out the $BaSO_4$. Concentrate this last filtrate and use it for the flame tests.

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[1] H_2PtCl_6 and $Na_3Co(NO_2)_6$ give rather difficultly soluble compounds with $\overset{\cdot}{K}$. $\overset{\cdot\cdot}{NH}_4$, however, gives exactly the same kind of precipitates with both reagents, so that in the hands of students, who are usually unsuccessful in expelling the last traces of ammonium salts, these tests for potassium are unreliable.

ACID ANALYSIS.

Acid analysis concerns itself with the detection of the acid radicals,[1] or negative ions (anions). The general method employed in testing for acid radicals differs very materially from that used in the detection of the metals. In the latter case the cations are precipitated in groups by certain group reagents, and the individual members of these groups are afterward separated from one another and identified. It is customary for the sake of classification to divide the anions into groups according to their behavior with certain precipitants, but the members of these groups are not then systematically separated from one another before being identified. The identification of most of them is effected without preliminary separation from the others, at least in any systematic manner. This can be accomplished on account of the much greater number of characteristic reactions exhibited by these ions than by the cations.

The anions are divided into the three following classes:

Sulphuric Acid Group.—Those which unite with $\overset{..}{Ba}$ to form a precipitate in a neutral solution: SO_4'', $[SiF_6'']$,[2] SO_3'', S_2O_3'', CrO_4'', PO_4''', CO_3'', SiO_3'', BO_2', AsO_3''', AsO_4''', C_2O_4'', $C_4H_4O_6''$, $[F']$.

Halogen Group.—Those which unite with $\overset{.}{Ag}$ to form a precipitate in a solution acidified with HNO_3: Cl', Br', I', CN', S'', $[NO_2',$[3] $ClO',$[4] SCN', $Fe(CN)_6'''$, $Fe(CN)_6''''$].

Nitric Acid Group.—Those not precipitated in either of the above cases: NO_3', NO_2', ClO_3', $C_2H_3O_2'$.

Note 1.—Acids are also classed as organic[5] and inorganic. The anions of organic acids in the above list are $C_4H_4O_6$, $C_2H_3O_2'$, C_2O_4''. All the rest are inorganic. When heated at a high temperature the first two of these char, but C_2O_4 does not. It is, however, burned up and removed by the

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[1] It is to be emphasized that the substance to be tested contains acid radicals and almost never free acids, so that it is the radicals we wish to identify. Students frequently acquire an erroneous impression upon this point.

[2] Those in brackets occur very seldom and may be omitted in a brief course.

[3] Precipitated only from concentrated solutions, so that it is usually classed with the next group.

[4] Gives a precipitate here because it always contains chloride.

[5] The majority of organic acids lie outside the scope of this book.

process for destroying organic matter (see closed-tube test, p. 66; also Note 1, p. 71).

2. A knowledge of the solubility of a substance and the metals it contains frequently restricts the number of acids to be looked for, e.g., if a substance is soluble in water and Pb has been found it is useless to test for SO''_4, since $PbSO_4$ is insoluble. In what follows (p. 70 et seq.) provision has been made for examining the aqueous solution of any mixture for both positive and negative radicals, so that a knowledge of the solubility of different substances will be of great service. The following statements may aid in this.[1]

(a) All ordinary salts of Na, K, Li and NH_4 are sufficiently soluble in water so that they will be found in aqueous solution prepared according to the methods of pp. 70–73. For an exception see bottom of p. 73.

(b) All nitrates, nitrites, chlorates, and acetates are soluble in water except some basic nitrates and acetates.

(c) All carbonates, phosphates, borates, oxalates, tartrates, arsenates, arsenites, except those of the alkali metals are insoluble in water, but are dissolved by dilute acids.

(d) All chlorides, bromides, and iodides except those of lead, silver, mercurous mercury, and cuprous copper, and HgI_2 are soluble in water; likewise all sulphates except those of barium, strontium, calcium, and lead.

3. If the substance to be analyzed is a mineral it is useless to test it for organic acids or for cyanogen acids.

PRELIMINARY TESTS.

1. *General.*—Cover a little of the solid substance with concentrated H_2SO_4 in a very small test-tube and warm gently (do not boil). Note odor and any characteristic color.

Sulphates, phosphates, and chromates give no indication.

Silicates may separate flocculent H_2SiO_3.

Sulphites evolve SO_2.

Thiosulphates evolve SO_2 and separate S in a very finely divided state (white).

Carbonates and oxalates cause effervescence due to escape of CO_2,[2] accompanied in the case of oxalates by CO.

Tartrates likewise cause effervescence, but in addition they give an odor resembling that of burnt sugar, and cause blackening of the acid.

Acetates evolve acetic acid with the odor of vinegar.

Chlorides evolve HCl, sharp, pungent odor.

[1] See also inside back cover.

[2] If this test is obtained, cover a fresh portion of the substance with dilute HCl· Copious effervescence, clouding lime-water, indicates a carbonate. Oxalates give no indication in this case.

Bromides evolve HBr and Br_2, brown color, characteristic odor.

Iodides separate iodine, on sufficient heating a violet-colored gas is evolved.

Fluorides (care!) evolve HF, etches glass.

Cyanides (care!) evolve HCN, odor of bitter almonds.

Sulphides, those which are decomposable evolve H_2S.

Nitrates evolve HNO_3, colored slightly brown by small amount of NO_2.

Nitrites evolve copious brown fumes of NO_2.

Chlorates evolve ClO_2 (explosive) and Cl_2.

Hypochlorites evolve Cl_2.

Note.—The first action is one of double decomposition, setting free the acid of the salt. The acid so liberated may be stable, may be unstable in itself, or may be decomposed by the sulphuric acid.

2. *Sulphuric Acid Group Test.*—Make the solution for the acid analysis acid with HCl, warm a little and observe whether any turbidity results. Such turbidity is due to S and indicates a thiosulphate or a polysulphide.[1] Continue filtering until clear.

a. To the clear solution add $BaCl_2$ solution.

A white precipitate indicates SO_4'' [or SiF_6''].

b. Filter, and to the filtrate add $CaCl_2$ solution and an equal volume of N $NaC_2H_3O_2$ or one-fourth the volume of $4N$ $NH_4C_2H_3O_2$.

A white precipitate indicates C_2O_4'', SiO_3'' [or F']. A yellow one, CrO_4''.

c. Filter, and make the filtrate just alkaline with $Ba(OH)_2$ solution.

A white precipitate indicates[2] PO_4''', AsO_4''', AsO_3''', SO_3'',[3] $C_4H_4O_6''$, BO_2'.

Note.—$CaCl_2$ is added because the oxalate and tartrate of calcium are less soluble than the corresponding barium salts.

[1] Some sulphides in the presence of oxidizing agents also give a separation of S here.

[2] Carbonates belong to this division of the group, but are destroyed in this test by the preliminary acidifying with HCl.

[3] Sulphites may likewise be destroyed on acidifying with HCl, especially if the solution was boiled while acid. Sulphites are, however, almost always accompanied by sulphates on account of partial oxidation. If, therefore, only a trace of SO_4'' is indicated, it may be due to sulphite, or thiosulphate even, in the original substance.

2. The addition of $NaC_2H_3O_2$ greatly decreases the acidity of the solution (see p. 5). If the solution is concentrated precipitates containing the ions under *c* may be obtained when $NaC_2H_3O_2$ is added.

3. Barium borate does not precipitate very readily, and hence borates may be present even when no precipitate is obtained at this point. Furthermore, ammonium salts may interfere with the precipitation of some of the salts of the other radicals, especially of the tartrate. Consequently borates or tartrates may be present even when no precipitate is obtained here.

3. *Silver Nitrate Test.*—(A) Acidify a fresh portion of the solution for the acid analysis with HNO_3 and add $AgNO_3$ solution.

A white precipitate indicates Cl′, CN′, [ClO′, SCN′, $Fe(CN)_6'''$, or $Fe(CN)_6''''$].

A yellowish white precipitate indicates Br′.[1]

A yellow precipitate indicates I′.

A black precipitate indicates S″.[2]

If a precipitate is obtained, shake violently, allow to settle, and pour off the liquid carefully through a filter-paper without disturbing the precipitate. Treat the filtrate, or the solution in which no precipitate was obtained, according to (B). Wash the precipitate by decantation, add dilute NH_4OH,[3] and shake thoroughly. If the precipitate dissolves, Br′, I′, S″ [SCN′, and $Fe(CN)_6''''$)] are excluded.

In the filtrate from the previous treatment additional information may frequently be obtained with regard to the radicals of the Sulphuric Acid group, for all of them except SO_4'' and F′ give precipitates with Ag in a neutral solution. The procedure is as follows:

(B) Add additional $AgNO_3$ solution to the filtrate to make sure that the precipitation of the Halogen group is complete. Filter out any additional precipitate, and into this filtrate, or into the solution in which $AgNO_3$ solution produces no further precipitate, allow NH_4OH to run carefully so as to form a layer on top. Observe the color of any precipitate or film formed at the neutral zone.

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[1] If the solution is dilute, the precipitate may be almost white.

[2] Thiosulphates, if present, are apt to be decomposed by the HNO_3 liberating S, which may give a black precipitate here.

[3] AgBr and AgSCN are soluble in excess of conc. NH_4OH. Hence the reason for using the dilute reagent here.

Indications:

Yellow: Ag_3PO_4 and Ag_3AsO_3.

Dark red: Ag_2CrO_4.

Brick red: Ag_3AsO_4.

White: $Ag_2C_2O_4$ and $Ag_2C_4H_4O_6$.

A white cloudiness turning to yellow and finally to brown may be due to borates or carbonates, which are considerably hydrolyzed by water, and hence precipitate some Ag_2O.

Silver sulphite and nitrite are so soluble that they usually give no indication.

4. *No Group Reagent.*—Whether or not precipitates have been obtained with tests 2 and 3, just preceding, members of the Nitric Acid group may be present, viz., NO_3', ClO_3', $C_2H_3O_2'$, (and NO_2'). Special tests should therefore be made for them.

Note.—For reasons heretofore given (Note 3, p. 55) tests should also be made for $C_4H_4O_6''$ and BO_2', even though no preliminary indication of them has been obtained.

SPECIAL TESTS.

Special tests for acid radicals, the absence of which has not been definitely indicated by the Preliminary tests, are then made according to the following directions. They are arranged in alphabetic order. "The solution" in the following tests signifies the solution for the acid analysis as prepared according to directions on pp. 74–5, unless a different solution is specified.

Acetates, $C_2H_3O_2'$.

The odor of vinegar obtained in Preliminary test 1, p. 53, is one of the best indications.

It is confirmed as follows: Treat an aqueous solution of the substance with 2 c.c. amyl alcohol[1] and 5 c.c. conc. H_2SO_4, shake together, and warm gently. Characteristic banana odor indicates an acetate.

Note.—Amyl acetate, $C_5H_{11}C_2H_3O_2$, is formed.

Arsenates, AsO_4'''.

Arsenates respond to both of the tests for phosphates, p. 63. Great care must therefore be exercised to distinguish between them. If arsenic has been found in the Basic Analysis, it is very likely present in the original substance in the form of an arsenate or arsenite.

Arsenates are indicated in the test 2 (B), p. 55. Confirm by acidifying the prepared solution with conc. HCl, warming, and passing H_2S through the solution. A slight yellow precipitate, As_2S_5, forming very slowly, indicates an arsenate.

Arsenites, AsO_3'''.

(Read under arsenates, just above.)

An indication of this radical is given in test 2 (B), p. 55. Other tests are:

1. Acidify the solution with conc. HCl, and pass H_2S through the solution exactly as above in the case of arsenates. A copious yellow precipitate, As_2S_3, indicates an arsenite.

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[1] Ordinary ethyl alcohol may be used instead of amyl alcohol, but in this case the student is less apt to distinguish between the odor of the alcohol and that of the ethy acetate.

2. Add some Fehling's solution to a portion of the solution, and allow to stand in a hot water-bath for several minutes. The appearance of a reddish precipitate, Cu_2O, indicates an arsenite.

Note.—The arsenite reduces the cupric compound in solution precipitating cuprous oxide.

Arsenates in the Presence of Arsenites.

To the solution add a little potassium iodide and starch solution, and acidify with HCl. A blue color indicates an arsenate (in the absence of other oxidizing acids as H_2CrO_4 and HNO_2).

Borates, BO'_2.[1]

1. Place some of the solid substance in a test-tube fitted with stopper and tubes as in the accompanying figure. Mix thoroughly with conc. H_2SO_4, and add a little methyl alcohol. Warm the mixture, and blow with a small bellows through the tube which projects below the liquid, so that the vapor expelled through the other tube will be ejected either into the opening at the base of a Bunsen burner or directly into the flame itself. If the flame of the Bunsen burner is colored green, a borate is indicated. (Neither copper salts, barium salts, nor fluorides interfere with the test when carried out in this manner.)
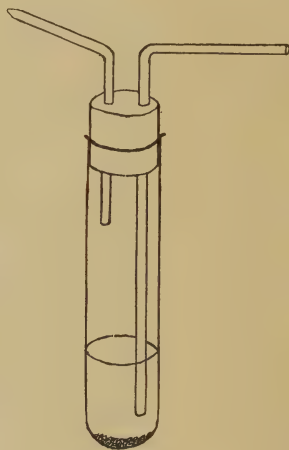
Note.—A volatile ester, $(CH_3)_3BO_3$, is formed, which passes over and burns with a green flame.

2. Acidify the solution very slightly with dilute HCl.[2] Dip a piece of turmeric paper partly into the liquid. Dry the paper on a watch-glass. A pinkish or reddish tint indicates a borate.

[1] The formula of boric acid is H_3BO_3, but only one of the three H atoms is replaceable. Many of its insoluble salts, *e.g.*, $AgBO_2$, are derived from the meta acid, HBO_2, and hence the anion will always be written BO'_2.

[2] HCl in any quantity interferes with this test, as it turns the turmeric paper brown.

Bromides, Br'.

1. The test with $AgNO_3$ solution is an indication (see p. 55). The precipitate darkens on exposure to the light.

2. Add to the slightly acid solution a few drops of carbon disulphide, then a little chlorine water, and shake. If the drops of carbon disulphide become brown, a bromide is indicated.

Note.—In the presence of an iodide, iodine will also be liberated. In such a case continue the addition of chlorine water drop by drop until the violet color of the iodine has just disappeared. If a brown color remains, a bromide is indicated. Chlorine oxidizes iodine to ICl_3.

Carbonates, CO_3''.

The test for this acid radical has already been given, footnote 2, p. 53.

Indications of carbonates are also obtained in preparing the solution for the Basic Analysis, provided acids have been used in the process (see p. 70).

Chlorates ClO_3'.

A good indication of these is usually obtained in Preliminary test 1, pp. 53–4.

1. Halogen acids must first be removed, if present, by acidifying the solution with HNO_3, and then adding $AgNO_3$ solution. To the filtrate, or to the solution containing no halogen acids, add a few drops of $AgNO_3$ solution and then pure KNO_2. A white curdy precipitate of $AgCl$ indicates a chlorate.

Note.—Nitrous acid reduces chlorates to chlorides. One must be sure that the KNO_2 is free from chlorides.

2. If no halogen acids are present, heat some of the solid substance in a closed tube of hard glass to a high temperature. Break the tube, extract the residue with hot water, acidify with HNO_3, and test the solution (which must be clear) for Cl' with $AgNO_3$ solution.

Chlorides, Cl'.

1. The $AgNO_3$ test, p. 55, is usually sufficient for this radical, provided the precipitate is curdy and darkens rapidly on exposure to the light. Cyanides and thiocyanates give white precipitates

with $AgNO_3$. They differ, however, somewhat from AgCl in appearance and do not darken so readily on exposure to light.

2. In case bromides and iodides are present, chlorides must be tested for as follows: Mix in a mortar some of the solid substance and some $K_2Cr_2O_7$, transfer to a small distilling flask, cover with conc. H_2SO_4, and warm, causing the vapors evolved to pass into a small test-tube containing dilute NH_4OH (look out for sucking back). A yellow color imparted to the solution due to the formation of $(NH_4)_2CrO_4$ indicates a chloride.

Note.—The yellow color will appear at once if chlorides are present, so long continued heating is unnecessary. CrO_2Cl_2, b. p. 116°, is formed and distils over. It is decomposed by water into $2HCl$ and H_2CrO_4, the latter combining with the NH_4OH. Bromine and iodine do not form similar compounds with chromium. They will distil over in elementary form, and combine with the NH_4OH to form colorless compounds.

Chromates CrO_4''.[1]

1. Reducing agents in the presence of free acids change chromates into green chromium salts.[2]

2. In case sulphates, phosphates, oxalates, and tartrates are absent, acidify the solution slightly with HNO_3, boil to remove CO_2 if necessary, then add considerable $NaC_2H_3O_2$ solution and a few drops of $Pb(C_2H_3O_2)_2$ solution. A yellow precipitate, $PbCrO_4$, indicates a chromate.

If any of the above salts are present, after removing CO_2, make the solution just alkaline with NH_4OH, and add a little $CaCl_2$ solution. Warm gently, and let stand 15 minutes, shaking from time to time. Filter, acidify the filtrate with HNO_3, add $BaCl_2$ solution, shake thoroughly, and filter off any precipitate. Treat the filtrate with $NaC_2H_3O_2$ solution. A yellow precipitate occurring at once, $BaCrO_4$, or upon the addition of $Pb(C_2H_3O_2)_2$ solution, $PbCrO_4$, indicates a chromate.

Note.—$CaCl_2$ precipitates PO_4''', C_2O_4'', and $C_4H_4O_6''$; $BaCl_2$ precipitates SO_4''. One or the other of these reagents can usually be omitted, depending upon the kinds of salts present.

[1] Dichromates, Cr_2O_7'', give the same tests.

[2] If chromates or dichromates are present, the introduction of H_2S to precipitate the Copper-Tin group causes the color of the solution to change from yellow or orange to green.

Cyanides, CN'.

1. To the solution (which must be alkaline; if not, make so with NaOH) add a little $FeSO_4$ solution and still less $FeCl_3$ solution. Warm the mixture for a few minutes on the water-bath shaking occasionally, finally acidify with HCl. Blue precipitate, $Fe_4(Fe(CN)_6)_3$, indicates a cyanide (*cf.* p. 22).

2. Place some of the substance in a distilling flask, add dilute H_2SO_4, warm gently, and catch any gas which comes over in a test-tube of water containing 1/2 c.c. yellow ammonium sulphide. Evaporate the contents of the test-tube to dryness on the water-bath, dissolve the residue in dilute HCl, and add a few drops of $FeCl_3$ solution. A red color, due to $Fe(SCN)_3$, indicates a cyanide.

Note.—H_2SO_4 liberates HCN, which distils over and is oxidized to HSCN by the extra S of the yellow ammonium sulphide.

Ferricyanides, $Fe(CN)_6'''$, and Ferrocyanides, $Fe(CN)_6''''$.

Test the solution acidified with HCl first with the solution of a ferrous salt, and a second portion with the solution of a ferric salt. For indications see Preliminary tests, p. 22. In addition it should be noted that Fe with ferrocyanides gives a very light blue precipitate and that Fe with ferricyanides gives a brown color. It must be borne in mind that all solutions of ferrous salts contain ferric also, unless the solution has been freshly prepared from metallic iron.

Fluorides, F'.

Cover a piece of glass with paraffin and scratch some design in the paraffin. Place some of the dry substance on the bottom of a lead dish, moisten with conc. H_2SO_4, stirring to a paste with a piece of wood (burnt match), and cover the dish with the glass, paraffin side down. Warm very gently from time to time, and allow the action to proceed for 15 to 20 minutes. Remove the paraffin. If the design is etched in the glass, a fluoride is indicated. (See L. C., 153; S. C., p. 171.)

Hypochlorites,[1] ClO'.

1. Treat the solid substance with dilute HCl, chlorine will be evolved recognized by its odor.

[1] It is useless to test for hypochlorites unless chlorides are present, as the latter always accompany hypochlorites.

2. Make the *aqueous* solution alkaline with Na_2CO_3, add 4 or 5 drops of acetic acid (not enough to make solution acid), and then introduce a piece of litmus-paper. Bleaching of the color indicates a hypochlorite.

Iodides, I'.

Make the solution acid with HCl, add a small piece of KNO_2 and a few drops of carbon disulphide, and shake. A violet color imparted to the globule of carbon disulphide indicates an iodide.

Nitrates, NO_3'.

Mix the concentrated solution, which should be acid, with an equal volume of $FeSO_4$ solution, and then allow conc. H_2SO_4 to run down the side of the inclined test-tube so as to form a layer on the bottom. A dark brown ring at the junction of the two layers, which disappears readily on shaking, indicates a nitrate (in the absence of nitrites). See L. C., p. 212; S. C., p. 296.

Note.—Chlorates, chromates, bromides, and iodides interfere with this test for nitrates, and must therefore be removed, if they are present, before this is attempted.

Chlorates are destroyed by mixing the solid substance with dry Na_2CO_3, and then heating to a high temperature in a porcelain dish for 5 to 10 minutes. Cool, extract the residue with hot water, and use this solution for the above test.

Chromates are removed by adding H_2SO_3 to the solution and warming until the color becomes quite green. Then add NH_4OH to slight excess to precipitate the chromium, boil, and filter. Test the filtrate as above directed.

Bromides and iodides are removed by acidifying slightly with H_2SO_4 and then adding a saturated solution of Ag_2SO_4 as long as a precipitate continues to fall. Filter, and test filtrate for nitrates as above.

Nitrites, NO_2'.

These give the same test as nitrates, but the brown ring is much more prominent and does not disappear so readily on shaking. Nitrites also give the test, when acetic acid is used instead of sulphuric, while nitrates do not. In this case, however, the whole solution usually becomes dark colored.

Nitrites will reduce an acidified solution of $KMnO_4$ or oxidize an acidified solution of KI (see test for iodides). These tests are not certain, however, if other oxidizing or reducing agents are present.

See also distinction in Preliminary test 1, pp. 53–4.

Oxalates, C_2O_4''.

Acidify some of the solution with acetic acid, warm, and add an equal volume of a saturated solution of $CaSO_4$. A white precipitate is probably CaC_2O_4. Confirm as follows: Filter, and wash thoroughly. Dissolve the precipitate in warm dilute H_2SO_4, and add a drop of dilute $KMnO_4$ solution. If the permanganate is bleached, an oxalate is indicated.

Note.—Permanganates oxidize $H_2C_2O_4$ to CO_2 and H_2O.

Phosphates, PO_4'''.

Arsenates must first be known to be absent, as they respond to both of these tests. If this radical is present it is removed by acidifying, warming, and then passing in H_2S as long as a precipitate continues to fall. Filter and expel the H_2S from the filtrate by boiling.

1. Acidify a little of the solution with HNO_3, then add the solution drop by drop to 5 c.c. ammonium molybdate solution in a test-tube.[1] If no precipitate appears at once, warm to $40°$ and allow to stand for a few hours. A yellow precipitate, $(NH_4)_3PO_4 11MoO_3 6H_2O$, indicates a phosphate.

2. If the solution is alkaline with Na_2CO_3, make just acid with HCl, and then add considerable NH_4OH. If a precipitate forms, filter it off, and to the filtrate add a little magnesia mixture. Stir with a glass rod, and, if no precipitate forms, allow to stand for several hours. A white crystalline precipitate, NH_4MgPO_4, indicates a phosphate.

Silicates, SiO_3''.

1. In case a silicate is suspected, make the test with the microcosmic bead, p. 69, note.

2. Mix some of the dry substance in a mortar with an equal quantity of CaF_2. Transfer to a platinum crucible, moisten with conc. H_2SO_4, and heat gently under the hood, holding a loop of platinum containing a drop of water at the mouth of the crucible. A white gelatinous deposit, H_2SiO_3, in the water indicates a silicate. (See L. C., p. 153; S. C., p. 345.)

Silicofluorides, SiF_6''.

Dry the precipitate obtained with $BaCl_2$ in Preliminary test 2.

[1] An excess of the solution supposed to contain a phosphate must be avoided, as the precipitate is soluble in an excess of phosphoric acid.

Place it in a small test-tube, cover with conc. H_2SO_4 and warm, holding at the mouth of the test-tube a loop of platinum wire containing a drop of water. A white gelatinous precipitate, H_2SiO_3, in the water indicates a silicofluoride. (See reference above.)

Sulphates, SO_4''.

The $BaCl_2$ test in Preliminary test 2, p. 54, is conclusive, unless silicofluorides are present. In this case confirm as follows: Dry the precipitate, mix with Na_2CO_3, and heat on charcoal before the blowpipe. Place the residue on a silver coin, crush it to a powder, and add a drop of water. A black stain indicates a sulphate.

Sulphides, S''.

1. Place some of the solid substance in a test-tube, cover with HCl, and warm, holding a piece of paper moistened with lead acetate solution at the mouth of the tube. A black stain on the paper and the characteristic odor of H_2S indicate a sulphide.

2. Some sulphides are not decomposed by HCl. These must be fused on a porcelain fragment with NaOH. Place the residue on a silver coin, crush to a powder, and moisten with a drop of water. A black stain on the coin indicates a sulphide, in the absence of thiosulphates or sulphates accompanied by organic matter.

Indications of the presence of sulphides are also obtained while preparing the solution for the Basic Analysis (see p. 70).

Sulphites, SO_3'', and Thiosulphates, S_2O_3''.

If either of these has been indicated in Preliminary test 1, p. 53, repeat the test in a larger test-tube with *dilute* H_2SO_4. (See also under test 2, p. 54.) A trace of sulphate almost always accompanies these salts on account of incipient oxidation.

Both sulphurous and thiosulphuric acid are reducing agents. Acidified solutions of their salts will therefore decolorize iodine water.

Tartrates, $C_4H_4O_6''$.

The indication given in Preliminary test 1, pp. 53–4, is reliable provided organic matter other than acetates and tartrates is absent.

If, however, charring has been observed in the closed-tube test, p. 66, and the presence of other organic matter is uncertain, tartrates should be identified by one of the following tests:

1. Prepare a solution by boiling some of the solid substance with K_2CO_3 for a few minutes and filtering. Evaporate the filtrate until solid matter begins to separate out, add a drop or two of water to get everything into solution again, and acidify carefully with acetic acid. Cool, shake violently, and, if a precipitate does not appear, add an equal volume of alcohol, and let stand for 15 minutes shaking occasionally. Filter off any precipitate obtained at first or on the addition of alcohol, which is probably $KHC_4H_4O_6$, wash with a little ether and dry thoroughly. Now remove the precipitate to a test-tube, dissolve it in a few drops of KOH, and add a little $AgNO_3$ solution. Dissolve the precipitate thus formed in NH_4OH. Place the test-tube in a hot water-bath, and evaporate almost to dryness. A silver mirror on the test-tube indicates a tartrate. (Many organic substances thus reduce compounds of silver; see L. C., p. 303; S. C., p. 421.)

2. Mix some of the solution in a test-tube with an equal volume of NaOH solution (or treat the solid substance directly with NaOH, boil, cool, and filter; use the filtrate), add a few drops of $CuSO_4$ solution, shake for several minutes, and filter until transparent. If the filtrate is blue, a tartrate is indicated. If not blue, add a few drops of NH_4OH. The development of a blue color indicates a tartrate.

Note.—An alkaline solution of tartaric acid dissolves copper hydroxide, the Cu replacing the H of the alcoholic radicals.

Thiocyanates, SCN′.

Acidify the solution with HCl, and add $FeCl_3$ solution. A deep red color, due to $Fe(SCN)_3$, indicates a thiocyanate.

The color should disappear on the addition of $HgCl_2$ solution.

ANALYSIS IN THE DRY WAY.

When the substance to be analyzed is a solid, it is usual to subject it first to a few simple dry tests before proceeding to the systematic analysis which has been given in the preceding pages.

In the hands of an expert these dry tests frequently yield information, which enables one to select at once the method to be used in preparing the solution for the Basic Analysis (p. 70 *et seq.*), and also which may permit a material shortening of the subsequent processes of analysis. In the hands of the beginner these results cannot be attained at once. His conclusions should be tentative, never final, ready to be modified by the results of the subsequent analysis. As his experience becomes greater he will gradually learn to select from a mass of seemingly contradictory observations the ones which are most important and which are of direct help in indicating the methods to be employed later. In general, the results of the bead and flame tests are more definite and are more to be relied upon than those of the closed-tube and blowpipe tests, especially in the hands of an inexperienced person.

CLOSED-TUBE TEST.

Place a small portion of the substance in a closed tube of hard glass, and heat at first gently and later to the highest temperature of the Bunsen flame.

Note whether water is evolved by gentle heating, and if so, test its reaction with litmus-paper. If a gas seems to be given off, note its odor, whether it causes a glowing splinter to ignite, and whether it clouds lime-water (this should be done while the heat is being increased, as the gas may all be expelled before the highest temperature is attained).

Indications:

1. Water evolved in considerable quantity indicates water of crystallization; in smaller quantity it may be due to water of constitution or to water mechanically enclosed within the crystals. (In general, water of constitution is liberated only at the higher temperatures.) If the water evolved is acid in reaction, the acid of the salt is volatile; if alkaline, some ammonium salt is probably present.

2. If the substance chars and smells of burnt matter, an

organic substance is indicated; tartrates or acetates in the absence of other organic matter.

Note.—Blackening alone does not indicate the charring of an organic substance unless accompanied by the characteristic odor.

· 3. Change of color.

Salts of Cu, Ni, Co, and Mn change to black or dark brown, color of the oxides.

Salts of Fe change to dark red, color of ferric oxide.

Some salts of Hg change to black, hot; dark red, cold, and yield drops of Hg.

S free, or in polysulphides, melts to a brown liquid, with odor of SO_2.

$PbCrO_4$ and the alkali chromates are dark red and fusible, hot; yellow, cold.

Most of the oxygen salts of Pb, Bi, Sn, and Zn are changed to the oxides, which show the following changes:

PbO, yellowish-red, hot; yellow, cold; fusible and unites with the glass.

Bi_2O_3, orange, hot; light yellow, cold; fusible.

SnO_2, yellowish-brown, hot; dirty white, cold.

ZnO, yellow, hot; almost white, cold.

4. Evolution of a gas.

Oxygen indicates a chlorate, nitrate, or peroxide.

Chlorine indicates chlorides with oxidizing agents, or a hypo-chlorite.

Bromine indicates bromides with oxidizing agents.

Iodine indicates iodides with oxidizing agents.

NO_2 indicates a nitrate or nitrite, except those of K, Na, Li, and NH_4.

SO_2 indicates a sulphate, sulphite, or burning S.

CO_2 indicates carbonates, organic acids, or other organic matter.

CO indicates oxalates and some other organic substances.

NH_3 indicates some ammonium salt.

H_2S indicates a sulphide, or S with a reducing agent.

5. Formation of a sublimate.

White crystalline, may be $HgCl_2$, As_2O_3, Sb_2O_3, or an ammonium salt.

White, yellow when hot, may be HgCl.

Yellow, may be As_2S_3.

Yellow, red when rubbed, may be HgI_2.

Black, may be arsenic.

Dark purple with violet vapor, may be iodine.

Dark red when hot and quite fusible, may be sulphur.

Black, red when rubbed, may be HgS.

Metallic globules, probably mercury.

BLOWPIPE TEST.

Heat some of the substance in a small cavity of a piece of charcoal before the reducing[1] flame of the blowpipe. Observe any changes which take place and the color of any incrustation or residue. Place a little Na_2CO_3 on any residue and heat again. Indications:

1. Deflagration indicates a chlorate or a nitrate.

2. If the substance fuses and is then absorbed by the charcoal, it is probably a salt of one of the alkali metals.

3. A white infusible residue may be an oxide of Ba, Sr, Ca, Mg, Al, or Zn. On moistening with a drop or two of $Co(NO_3)_2$ and heating again, Al_2O_3 turns blue, ZnO turns green.

4. Metallic globule without incrustation[2]:

Silver, Tin, Copper, and sometimes Cobalt, Nickel, and Iron.

5. Metallic globule with incrustation:

Globule.		*Incrustation.*
Antimony,	Brittle,	White, hot and cold.
Cadmium,	Malleable and soft,	Dark orange, hot and cold.
Lead,	Malleable and soft,	Yellowish-red, hot; yellow, cold.
Bismuth,	Brittle,	Orange, hot; light yellow, cold.

With insufficient treatment only the incrustation may appear.

6. Incrustation without metallic globule:

HgCl, $HgCl_2$, and some ammonium salts, white.

As_2O_3,   white with garlic odor.

ZnO,   yellow, hot; white, cold.

[1] Obtained by blowing gently so as just to turn the luminous flame over on the substance.

[2] An incrustation is a film-like deposit more or less removed from the cavity.

BEAD TEST.

Make a borax bead in the loop of a clean platinum wire, place upon it a minute quantity of the solid substance, and heat either in the Bunsen flame or before the blowpipe. Note the color when cold.

Substance.	In the Oxidizing Flame.	In the Reducing Flame.[1]
Cobalt,	Blue,	Blue.
Copper,	Greenish-blue,	Reddish, opaque.
Chromium,	Green,	Green.
Iron,	Yellow to colorless,	Green to colorless.
Manganese,	Violet,	Colorless.
Nickel,	Brown,	Gray.

Note.—If a silicate is suspected, make a bead of microcosmic salt, $NaNH_4$-HPO_4, and then proceed with the test as before. The colors given by the metallic oxides are the same as above; but, if a silicate is present, silica, SiO_2, floats around in the bead as an insoluble but semitransparent skeleton.

FLAME TEST.

Moisten a little of the solid substance with HCl, and make a flame test with a clean platinum wire.[2] If the yellow sodium flame is prominent, use a blue glass (see p. 50) in testing for potassium.

Substance.	Flame Color.
Potassium,	Violet or purple.
Sodium,	Yellow.
Lithium or strontium,	Red.
Calcium,	Orange.
Barium, Copper, or H_3BO_3,	Green.

[1] The student usually experiences considerable difficulty in obtaining these colors on account of inability to produce continuously a good reducing flame.

[2] To clean the platinum wire, dip it into commercial HCl and then hold it in the Bunsen flame. Continue this alternately until no color is imparted to the flame.

PREPARATION OF SOLUTIONS. ·

1. FOR THE BASIC ANALYSIS.

Before trying to get a solid substance into solution, the dry tests, pp. 66–69, and test 1, p. 53, should be made. ·

If evidence of organic matter appear, consult Note 1 below.

It should be borne in mind that much important information regarding the presence of several acid radicals may be obtained during the following treatment. For example, HCl may cause the liberation of CO_2, H_2S, SO_2, or HCN; HNO_3 of CO_2 or of free S from sulphides; aqua regia of free S from sulphides not decomposable by single acids.

SALTS AND OXIDES.

Treatment with Water.

Finely pulverize the substance in a mortar, and weigh out 1 gram of it. Cover this with about 40 c.c. water in a very large test-tube, heat, allow any residue to subside, and decant the liquid carefully through a filter-paper. If it is not perfectly evident that solution has taken place, evaporate a little of the filtrate to dryness on a platinum foil. If a residue remains on the foil, repeat the treatment with water as long as anything continues to dissolve. Combine the aqueous solutions thus obtained, and proceed with the analysis according to pp. 22–51.

Treatment with Acids.

If the dry tests have indicated the presence of either Pb or Ag, treat the residue remaining from the water treatment according to (b); if these metals are absent, according to (a).

(a) Pour 10 c.c. dilute HCl over the residue, and warm. If solution is not complete, add 5 c.c. conc. HCl without filtering, and warm as long as anything appears to dissolve, replacing the acid lost by evaporation. If solution is not now complete, filter, and treat the residue with a little hot aqua regia. Any residue remaining is to be treated according to the directions, p. 72. Combine the HCl and the aqua regia filtrates, and evaporate almost

to dryness; add more conc. HCl, evaporate again, and so proceed until all the HNO_3 has been expelled. Dissolve in dilute HCl, dilute with water, and proceed with the basic analysis beginning with the separation of the Copper-Tin group, p. 28.

(b) Pour 10 c.c. dilute HNO_3 over the residue from the water treatment, and warm. If a residue remains, add 5 c.c. conc. HNO_3 without filtering, and heat again. If solution is not now complete, filter, and treat the residue with hot aqua regia. Dilute and filter, and treat any residue according to the directions on p. 72. Combine the HNO_3 and aqua regia filtrates. If a precipitate forms, filter it off, and analyze it for the Silver group, p. 26. Evaporate the filtrate, or the whole solution in case no precipitation occurred, nearly to dryness, add conc. HCl, and proceed with the expulsion of the HNO_3, and the analysis of the remaining solution exactly as in (a).

Note 1.—If organic matter is present, it must be removed, for it interferes with the tests for many of the cations, especially those of the Iron group. To accomplish this, mix 1 gram of the original solid substance with about 4 grams NH_4NO_3. Fuse some additional NH_4NO_3 in a porcelain crucible, add the mixture just prepared, and regulate the temperature so as to keep the mass in a state of gentle fusion. Continue heating until all carbonaceous matter is destroyed (indicated by quiet fusion); then heat to a little higher temperature to expel most of the remaining NH_4NO_3, cool, and proceed with the preparation of the solution as above. When this process is used, ammonium salts must be tested for in the original substance.

In the analysis of paints and substances of that nature containing organic matter, special methods of treatment should be used, for which consult some larger manual.

2.—Gelatinous silicic acid may separate during the treatment with acids. If this happens or if a silicate is known to be present, when expelling HNO_3 from the acid solution evaporate to dryness on a water-bath; then place in a drying oven at 125°, and heat for at least an hour. Dissolve the residue in a little dilute HCl, filter out the silicic acid, and proceed with the analysis of the solution in the usual manner.

Continued heating at 125° renders silicic acid insoluble in HCl. If heated to a higher temperature iron salts and some others might be converted into very insoluble oxides.

3.—The aqueous and acid solutions are analyzed separately because in many cases a precipitate may form if they are mixed, and further because more information is gained with regard to the composition of the original solid substance.

Residue Insoluble in Acids.

The residue[1] from the treatment with acids will belong to one or more of the following classes:

(*a*) Carbon, sulphur.

(*b*) $PbSO_4$, $PbCl_2$,[2] $AgCl$, $AgBr$, AgI.

(*c*) $CaSO_4$,[2] $SrSO_4$, $BaSO_4$, silicates.

(*d*) Al_2O_3, Cr_2O_3, Fe_2O_3, SnO_2, and basic salts of Sn.

(*e*) Some cyanides or ferrocyanides of the heavy metals, CaF_2.

The presence of (*a*), (*b*), or (*e*) should have been indicated in the dry tests, pp. 66–69, or in test 1, p. 53. If any uncertainty exists as to the presence of members of these groups, repeat dry tests, 1, 2, and 3 with some of the residue itself.

If members of (*a*) are present, remove them by ignition on a piece of porcelain.

If members of (*b*) are present, proceed as follows: Treat the residue with tartaric acid, make just alkaline with ammonia, boil a few minutes, filter. This dissolves the first two. Repeat the treatment until nothing more dissolves. The filtrate should be examined for $\overset{\cdot\cdot}{Pb}$, SO_4'' and Cl'. Treat any residue remaining with a concentrated solution of KCN. This dissolves the three silver salts. Examine the solution for $\overset{\cdot}{Ag}$ by adding a little $(NH_4)_2S$, filtering, washing, dissolving the precipitate in hot dilute HNO_3, and adding HCl to the clear solution. The halogen present may be detected by treating some of the residue with conc. H_2SO_4 in a small tube, as in Preliminary test 1, p. 53.

Any members of (*c*) are gotten into solution by fusion with Na_2CO_3. Members of (*a*) and (*b*) are first removed, after which the residue is mixed thoroughly with 4 or 5 times its weight of Na_2CO_3 and heated on the platinum foil[3] (if large in amount, in a platinum crucible) with the blast lamp for several minutes. After the mass is in a state of quiet fusion, remove the heat, and after cooling extract with hot water. Filter, and wash with hot water until free from alkali.

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[1] If more of the residue is needed, take 2 to 3 grams of the original substance and subject it to the treatment with acids.

[2] $PbCl_2$ and $CaSO_4$ are somewhat soluble in water, and may therefore have been removed by the previous treatment.

[3] Do not fuse on platinum until very certain that all reducible metals have been removed.

Residue:	Filtrate:
Carbonates of the metals. Dissolve in warm dilute HCl, and analyze for cations beginning with the Copper-Tin group, p. 28.	Sulphates, silicates, etc., of sodium.[1] If silicates are absent, use for the Acid Analysis in the same way as the solution prepared according to the directions on p. 74.

If silicates are present, evaporate one half of the filtrate to dryness on the water-bath, and ignite at 125° for an hour or two. Dissolve in a little dilute HCl, filter out the H_2SiO_3, and test the filtrate for $\overset{...}{Al}$ and $\overset{..}{Zn}$. Use the other half of the solution for the Acid Analysis.

Members of group (d) are fused with $KHSO_4$ at a moderate temperature[2] for some time. This decomposes Al_2O_3, Cr_2O_3, and Fe_2O_3, forming sulphates of the metals, which can be dissolved in water and identified in the usual manner. If SnO_2 or basic salts of Sn are present, fuse on charcoal before the blowpipe with a mixture of Na_2CO_3 and S. Remove the fused mass to a test-tube, boil with water, filter. Na_2SnS_3 is formed by the fusion, which is soluble in water. Acidify the filtrate with HCl, whereupon, if Sn is present, yellow SnS_2 will be precipitated.

If members of group (e) are present, treat with conc. H_2SO_4 in a platinum crucible. Test the escaping gases for HCN and HF. The resulting metallic sulphates, if not soluble in water, should be fused with Na_2CO_3 as with group (c).

Sodium and Potassium in Insoluble Silicates.

Although sodium and potassium silicates by themselves are soluble in water, when present in complex silicates they may be insoluble. In such a case proceed as follows: Boil some of the residue from the acid treatment, which is known to contain silicates, with conc. H_2SO_4. Let cool, dilute somewhat, and make the flame tests with some of the liquid without filtering (cf. p. 50).

[1] This filtrate may also contain Na_3AlO_3 or Na_2ZnO_2, in case silicates of Al or Zn were present.

[2] Too high a temperature must be avoided, as it will convert the sulphates into insoluble basic sulphates.

METALS AND ALLOYS

Cut the substance into very small pieces. Weigh out 1 gram, and heat with 15 c.c. conc. HNO_3 as long as any noticeable reaction continues.

If complete solution takes place,[1] add conc. HCl, filter off any precipitate, and analyze it for the Silver group. Evaporate the filtrate, or the solution in which no precipitate has appeared, nearly to dryness, add more conc. HCl, and evaporate again, and so continue until all HNO_3 has been expelled. Dilute, and proceed with the Basic Analysis.

If complete solution has not taken place, that is, a white residue[2] remains, filter it off, and proceed with the filtrate in the manner just described. Wash the residue thoroughly, and fuse it on charcoal with a mixture of Na_2CO_3 and S. Let cool, extract the mass with hot water, filter out any residue, and acidify the clear filtrate with HCl. Filter again, wash, and analyze the precipitate for the members of the Tin group, p. 34.

Note 1.—If the alloy is apt to contain P, test some of the nitric acid solution for phosphates by method 1, p. 63. In case Sn is also present, the P is probably in the insoluble residue as $Sn_3(PO_4)_4$. To detect it in such a case, acidify some of the filtrate after fusion above with HNO_3, filter, and use the filtrate for the phosphate test.

2.—Cr, Ba, Sr, and Ca are not present in alloys, and K and Na only in those which decompose water.

2. FOR THE ACID ANALYSIS.

Salts.

(*a*) If the aqueous solution of the substance contains no metals precipitated by Na_2CO_3,[3] use it for the tests for acid radicals.

If the aqueous solution does contain metals precipitated by Na_2CO_3, add this reagent to the aqueous solution until no further

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[1] A slight black residue, which is probably carbon or silicon, can be ignored. Sometimes such a residue may consist of Au or Pt. These will dissolve in aqua regia.

[2] This residue may contain SnO_2, Sb_2O_3, Sb_2O_4, or Sb_2O_5. As_2O_5 may also be retained by these.

[3] If ammonium salts are absent, Na_2CO_3 precipitates all of the metallic ions from a solution except As, Sb, and the alkalies. Mg is the only one held in solution by ammonium salts.

precipitation takes place, boil, and filter. Use the filtrate for the tests for the acid radicals (see parenthesis under (c) below).

When all of the original substance is not soluble in water, a solution for the acid analysis is obtained with the insoluble residue in one of the following ways:

(b) If the only heavy metals present in the residue can be precipitated by H_2S, suspend about 1 gram, finely divided, in water, warm, and pass in H_2S for 15 to 20 minutes, shaking frequently. Filter, boil the filtrate until H_2S is expelled, and use it for the acid analysis.

(c) If heavy metals not precipitated by H_2S are present in the residue insoluble in water, boil about 1 gram with a concentrated solution of Na_2CO_3 for several minutes (care! look out for bumping), and filter. Use the filtrate for the tests for acid radicals. (The extra Na_2CO_3 remaining in this solution must be destroyed by a suitable acid before most of the tests demanding a solution are made; e.g., acidify with HCl, boil to expel CO_2, and make as nearly neutral as possible with NH_4OH for test 2, p. 54; acidify with HNO_3 for test 3, p. 55; etc.)

All of the solutions obtained by the above methods are to be used for the acid tests, pp. 57–65, wherever a solution is required. It will be noted that there will be two such solutions for every substance only partially soluble in water.

Note.—It must not be forgotten that many of the tests for acid radicals are made with the original solid substance. Such tests, as for example, the one for carbonates, should always be tried, no matter what results are obtained with the tests carried out with these solutions.

Minerals and Metallurgical Products.

(a) Try the special tests for sulphides and carbonates with a little of the finely divided solid substance.

(b) Boil another portion with conc. HNO_3 for a few minutes, dilute, filter, and use the solution for test 1 for phosphates and for the test for chlorides with $AgNO_3$. If sulphides are absent, use it also for the $BaCl_2$ test for sulphates.

(c) If sulphides are present, boil some of the finely divided substance with a concentrated solution of Na_2CO_3, acidify the filtrate with HCl, and test for sulphates.

(*d*) Test for fluorides and borates with some of the solid substance. Remaining acid radicals likely to be present will be found in the solutions prepared for the basic analysis.

(*e*) If silicates are present, it is necessary to test for borates and fluorides as follows: Fuse 1 gram of the substance with 4 or 5 times its weight of Na_2CO_3, extract with hot water, and filter. Make test 2 for borates with a small portion of the filtrate. Then divide the rest of the filtrate into two portions. Evaporate one portion to dryness and make test 1 for borates with the residue. Acidify the other portion with acetic acid, allow it to stand, and filter off any precipitate. Add $CaCl_2$ to the filtrate, let stand, collect any precipitate on a filter-paper, and test it for fluorides in the manner indicated on p. 61.

APPENDIX.

REAGENTS IN SOLUTION.

ACIDS.

	Sp. g.	Concentration per cent.	Approximate normal concentration.
Hydrochloric Acid, saturated,	1.20	39.11	12.9N
concentrated,	1.13	25.75	8. N
dilute,	1.035	7.15	2. N
Nitric Acid, very concentrated,	1.42	69.80	15.7N
concentrated,	1.25	39.82	8. N
dilute,	1.07	12.33	2. N
Sulphuric Acid, concentrated,	1.84	95.60	36. N
dilute,	1.12	17.01	4. N
Sulphurous Acid, saturated solution of SO_2 in water,			3. N
Acetic Acid, glacial,	1.055	99.	17.6N
dilute,	1.032	23.2	4. N
Tartaric Acid, 150 g. in 1 liter,			2. N

ALKALIES.

Ammonium Hydroxide, or Ammonia,		
concentrated,	0.90	28.3 %NH_3, 15 N
dilute,	0.971	7.05%NH_3, 4 N

Potassium Hydroxide (contains approx. 20% water) 281 g. in 1 liter, 4 N
Sodium Hydroxide (contains approx. 10% water) 178 g. in 1 liter, 4 N

SALTS.

	Approximate normal concentration.	Grams in 1 liter of solution.
Ammonium Acetate, $NH_4C_2H_3O_2$,	4 N	308.
Ammonium Carbonate, $(NH_4)_2CO_3$,	2 N	78, and 40 c.c. conc. NH_4OH.
Ammonium Chloride, NH_4Cl,	2 N	107.1
Ammonium Molybdate, $(NH_4)_2MoO_4$,	N	98, see next page.
Ammonium Oxalate, $(NH_4)_2C_2O_4$,	1/2 N	Saturated solution.
Ammonium Sulphate, $(NH_4)_2SO_4$,	N	66.
Ammonium Sulphide, $(NH_4)_2S$,	4 N	See next page.
Barium Chloride, $BaCl_2.2H_2O$,	N	122.2.
Barium Hydroxide, $Ba(OH)_2$,	1/3 N	Saturated solution.
Calcium Chloride, $CaCl_2$,	N	55.6.
Calcium Hydroxide (Lime-water), $Ca(OH)_2$,	1/22 N	Saturated solution.
Calcium Sulphate, $CaSO_4$,	1/33 N	Saturated solution.
Cobalt Nitrate, $Co(NO_3)_2.6H_2O$,	1/2 N	62.3.

	Approximate normal concentration.	Grams in 1 liter of solution.
Ferric Chloride, $FeCl_3.6H_2O$,	N	91,+a little HCl.
Ferrous Sulphate, $FeSO_4.7H_2O$,	N	139+a little H_2SO_4.
Lead Acetate, $Pb(C_2H_3O_2)_2.3H_2O$,	N	189.5,+a little $HC_2H_3O_2$.
Magnesia Mixture,	N	See below.
Mercuric Chloride, $HgCl_2$,	$1/2$ N	Saturated solution.
Nitroso-β-naphthol,	$1/15$ N	See below.
Potassium Bromide, KBr,	$1/2$ N	59.6.
Potassium Chromate, K_2CrO_4,	N	97.3.
Potassium Cyanide, KCN,	N	65.2.
Potassium Dichromate, $K_2Cr_2O_7$,	N	73.8.
Potassium Ferricyanide, $K_3Fe(CN)_6$,	$1/10$ N	11.0
Potassium Ferrocyanide, $K_4Fe(CN)_6$,	$1/10$ N	10.6.
Potassium Iodide, KI,	$1/2$ N	83.1
Potassium Permanganate, $KMnO_4$, for oxidizing,	$1/2$ N	15.8 .
Potassium Thiocyanate, KSCN,	$1/2$ N	48.6
Silver Nitrate, $AgNO_3$,	$1/4$ N	42.5.
Silver Sulphate, Ag_2SO_4,	$1/25$ N	Saturated solution.
Sodium Acetate, $NaC_2H_3O_2$,	4 N	328.
Sodium Carbonate, Na_2CO_3,	4 N	212 (572 g. Decahydrate).
Sodium Chloride, NaCl,	$1/2$ N	29.3.
Sodium Hypochlorite,	N	See below.
Sodium Phosphate, $Na_2HPO_4.12H_2O$,	N	119.
Stannous Chloride, $SnCl_2$,	$1/2$ N	See below.

SPECIAL METHODS FOR PREPARING CERTAIN SOLUTIONS.

Ammonium Molybdate.—Dissolve 72 g. molybdic oxide, MoO_3, in 150 c.c. conc. ammonia to which 150 c.c. water has been added. Pour this solution slowly with constant stirring into a solution made by diluting 250 c.c. HNO_3 (sp. gr. 1.42) with 500 c.c. water. Allow the mixture to stand for a few days, then decant the clear liquid carefully from any precipitate into a bottle, and dilute to 1 liter.

Ammonium Sulphide.—Saturate 150 c.c. conc. ammonia with H_2S, add another 150 c.c. ammonia, and dilute to 1 liter.

Ammonium Sulphide, Yellow.—Prepare a solution as for ammonium sulphide, and add 10 g. flowers of sulphur, shake frequently until dissolved.

Magnesia Mixture.—Dissolve 101.8 g. $MgCl_2.6H_2O$ and 107 g. NH_4Cl in about 400 c.c. water, add 400 c.c. conc. ammonia, and dilute to 1 liter.

Nitroso-β-Naphthol.—Dissolve 4 g. of the crystallized substance in 150 c.c. glacial acetic acid. After solution is complete add 150 c.c. water, let stand a few hours, and then filter out any

sediment.   The solution must be freshly prepared every three or four weeks.

Sodium Hypochlorite.—Pour 250 c.c. $4N$ sodium carbonate and an equal volume of water over 80 g. of bleaching powder. Digest on the water-bath with frequent stirring for 2 to 3 hours, then filter and dilute to 500 c.c.   The solution should be freshly prepared every month or two.

Stannous Chloride.—Dissolve 30 g. granulated tin in 50 c.c. HCl (sp. gr. 1.20), and dilute to 1 liter.   After the solution has cooled add a few pieces of tin, which must be renewed from time to time in case they dissolve.

SOLUTIONS FOR ANALYSIS.

These may be made up approximately $1/2$ N.   No special directions are required except in certain cases, hints concerning which will be found on pp. 15–16, especially in the footnotes. Another good method for preparing such solutions and giving them out will be found in an abstract of a paper by L. J. Curtman, *Science*, 1910, p. 318.

DEGREE OF DISSOCIATION OF ELECTROLYTES.

Calculated from their electrical conductivity.
The figures are for normal solutions at 18° unless otherwise indicated.

Acids.

	Fraction ionized.		Fraction ionized.
Nitric acid,	0.82	Phosphoric acid,	0.058
Nitric acid, conc. 69%,	0.10	Tartaric acid,	0.025
Hydrochloric acid,	0.78	Acetic acid,	0.004
Hydrochloric acid, conc. 39%,	0.14	Acetic acid, $N/10$,	0.013
Sulphuric acid,	0.51	Carbonic acid, $N/10$,	0.0017
Sulphuric acid, conc. 95%,	0.01	Hydrogen sulphide, $N/10$,	0.0007
Oxalic acid,	0.15	Boric acid, $N/10$,	0.0001
Sulphurous acid,	0.08	Hydrocyanic acid, $N/10$,	0.0001

Bases.

Potassium hydroxide,	0.77	Barium hydroxide,	0.69
Sodium hydroxide,	0.73	Ammonium hydroxide,	0.004

Salts.

Ammonium chloride,	0.74	Potassium sulphate,	0.53
Barium chloride,	0.58	Silver nitrate,	0.58
Calcium chloride,	0.58	Sodium acetate,	0.53
Calcium sulphate, $N/100$,	0.63	Sodium carbonate,	(0.40)
Cupric sulphate,	0.22	Sodium hydrogen carbonate,	(0.52)
Ferrous sulphate,	0.24	Sodium chloride,	0.68
Lead acetate,	0.34	Sodium chloride, $N/10$,	0.84
Mercuric chloride,	0.01	Sodium phosphate,	(0.45)
Potassium acetate,	0.64	Sodium sulphate,	0.45
Potassium chloride,	0.75	Zinc chloride,	0.48
Potassium nitrate,	0.64	Zinc sulphate,	0.24

The values in parenthesis are uncertain on account of hydrolysis.

OPTIONAL METHOD FOR PRECIPITATING THE IRON-ZINC GROUP.

(As hydroxides and sulphides insoluble in alkaline solution.)

4. To the filtrate from the Copper-Tin group, from which H_2S has been expelled, add 5 c.c. NH_4Cl, and then NH_4OH until *just* alkaline. Heat to boiling, and add $(NH_4)_2S$ a few drops at a time until no further precipitation occurs. Filter, and wash free from alkali with warm water containing NH_4Cl and H_2S.

Precipitate:	Filtrate:
$Al(OH)_3$, $Cr(OH)_3$, FeS, CoS, NiS, MnS, ZnS.[1] Analyze according to direction on the next page.	Ions of the following groups: $\overset{..}{Ca}$, $\overset{..}{Ba}$, etc. Boil down to 100 c.c., and then proceed with the precipitation of the calcium group, p. 46.

NOTES.

1. According to this method, the ions of the Iron and the Zinc groups are precipitated together. NH_4OH will precipitate the hydroxides of aluminium, chromium, and iron (ferric) completely. Manganese hydroxide is partially precipitated, and zinc hydroxide may be more or less completely thrown down. Hence the two groups cannot be satisfactorily separated by this method.

2. The subsequent addition of $(NH_4)_2S$ converts the hydroxides of iron and manganese into the sulphides. The sulphides of aluminium and chromium are completely hydrolyzed in contact with water and hence are not formed.

3. Consult also the notes, pp. 41, 43.

[1] In case PO_4''' or C_2O_4'' is present, the phosphates or oxalates of Ba, Sr, Ca, and Mg may also be precipitated here (see p. 82).

ANALYSIS OF THE IRON-ZINC GROUP.

4*a*. Treat the group precipitate in a casserole with cold dilute HCl, stir with a glass rod for 10 to 15 minutes, filter, and wash with water containing H_2S.

Precipitate:
CoS, NiS, $(Cr(OH)_3)$.[1]
Proceed according to 5*b*, *c*, and *d*, p. 44.

Filtrate:[2]
$AlCl_3$, $CrCl_3$, $FeCl_3$, $MnCl_2$, $ZnCl_2$.

4*b*. Make just alkaline with pure NaOH solution, add a little solid Na_2O_2, stir until the action ceases, then boil for a minute or two, filter, and wash.

Precipitate:
$Fe(OH)_3$, $Mn(OH)_3$ or $MnO(OH)_2$.

4*c*. Test for manganese as in 5*g*, p. 45.

Filtrate:
Na_3AlO_3, Na_2CrO_4, Na_2ZnO_2.

4*d*. Acidify a small portion of this filtrate with dilute H_2SO_4. The appearance of a blue color ($HCrO_5$) either at once, or after adding a few drops of H_2O_2, indicates the presence of chromium.

4*e*. Just acidify the rest of the filtrate with HCl, add 5 c.c. NH_4Cl, and heat to boiling. While boiling add, drop by drop, 5 to 10 c.c. NH_4OH, filter.

Precipitate, $Al(OH)_3$.
4*f*. Confirm by heating with $Co(NO_3)_2$ solution as in 4*d*, p. 42.

Filtrate, $Zn(NH_3)_4Cl_2$.
4*g*. Acidify with acetic acid (if CrO_4'' is present, remove it by adding $BaCl_2$ solution and filtering), and pass in H_2S. A white precipitate, ZnS, should be confirmed by heating with $Co(NO_3)_2$ solution as in 5*h*, p. 45.

[1] A little $Cr(OH)_3$ may fail to dissolve. It does not, however, interfere with the tests for cobalt and nickel.

[2] See tests for PO_4''' and C_2O_4'' before proceeding (pp. 37 and 82). The method of separation which follows is that recommended by Böttger. The troublesome separation with an emulsion of $BaCO_3$ is thereby avoided.

6

ANALYSIS OF THE IRON-ZINC GROUP IN THE PRESENCE OF PHOSPHATES OR OXALATES.[1]

In case the original solution was obtained from a solid substance by treatment with acids (p. 70), and, further, in case a precipitate was obtained on neutralizing with NH_4OH in the precipitation of this group, PO_4''' or C_2O_4'' may be present, and it is necessary to make tests for them in the filtrate of $4a$, p. 81. The tests are made with small portions of this filtrate exactly as directed on p. 37. If these ions are found to be present the filtrate may contain (see Note 1, p. 39):

$\overset{...}{Al}$, $\overset{...}{Cr}$, $\overset{..}{Fe}$, $\overset{..}{Mn}$, $\overset{..}{Zn}$, $\overset{..}{Ba}$, $\overset{..}{Sr}$, $\overset{..}{Ca}$, $\overset{..}{Mg}$, PO_4''', C_2O_4'', etc.

Before $\overset{..}{Ba}$, $\overset{..}{Sr}$, $\overset{..}{Ca}$ and $\overset{..}{Mg}$ can be separated, PO_4''' and C_2O_4'' must be removed.

A. PHOSPHATES.

Removal of PO_4''.—The remainder of the filtrate of $4a$ is boiled with 2 to 3 c.c. conc. HNO_3 to oxidize $\overset{..}{Fe}$ to $\overset{...}{Fe}$. Then add Na_2CO_3 solution drop by drop, stirring constantly until a precipitate forms which does not entirely dissolve. Just dissolve this precipitate in the minimum quantity of dilute HCl, and then add $FeCl_3$ until the solution has a light yellow color. Dilute with 125 c.c. hot water, heat to boiling, and add 10 c.c. $4N\,NH_4C_2H_3O_2$ solution. In case the yellow color of the solution is not apparent, add more $FeCl_3$ until it is. Boil a few minutes longer, and filter.

Precipitate:	Filtrate:
$FePO_4$.	$\overset{...}{Al}$, $\overset{...}{Cr}$, $\overset{...}{Fe}$, $\overset{..}{Mn}$, $\overset{..}{Zn}$, $\overset{..}{Ba}$, $\overset{..}{Sr}$,
Reject.	$\overset{..}{Ca}$, $\overset{..}{Mg}$, etc.
	Make slightly alkaline with NH_4OH, and add $(NH_4)_2S$ as long as a precipitate continues to fall, boil, and filter.

[1] Before proceeding here read the first paragraph, p. 37, and the notes, p. 39.

Precipitate:	Filtrate:
$Al(OH)_3$, $Cr(OH)_3$, FeS, MnS, ZnS. Dissolve in dilute HCl, and proceed as in $4b$, p. 81.	$\overset{..}{Ba}$, $\overset{..}{Sr}$, $\overset{..}{Ca}$, $\overset{..}{Mg}$, etc. Add $(NH_4)_2CO_3$, boil, and filter.

Precipitate:	Filtrate:
$BaCO_3$, $SrCO_3$, $CaCO_3$. Unite with the precipitate of the Calcium group, p. 46.	$\overset{..}{Mg}$, etc. Add Na_2HPO_4, and, if a precipitate is obtained, unite it with that of 7, p. 50.

B. OXALATES.

Removal of C_2O_4''.—This is effected exactly as described on p. 37. After filtration from the Na_2CO_3 treatment, there may be present:

Precipitate:	Filtrate:
$Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$, $MnCO_3$, $ZnCO_3$, $BaCO_3$, $SrCO_3$, $CaCO_3$, $MgCO_3$. Dissolve in dilute HCl, add NH_4Cl, make just alkaline with NH_4OH, boil.	C_2O_4'', and possibly AlO_3''', CrO_3''', or CrO_4'', etc. Treat as directed in B. Filtrate, p. 38.

Add $(NH_4)_2S$ little by little as long as a precipitate continues to form, filter.

Precipitate:	Filtrate:
$Al(OH)_3$, $Cr(OH)_3$, FeS, MnS, ZnS. Dissolve in dilute HCl, and proceed as in $4b$, p. 81.	$\overset{..}{Ba}$, $\overset{..}{Sr}$, $\overset{..}{Ca}$, $\overset{..}{Mg}$, etc. Add $(NH_4)_2CO_3$, boil, and filter.

Precipitate:	Filtrate:
$BaCO_3$, $SrCO_3$, $CaCO_3$. Unite with the precipitate of the Calcium group, p. 46.	$\overset{..}{Mg}$, etc. Add Na_2HPO_4, and, if a precipitate is obtained, unite it with that of 7, p. 50.

C. PHOSPHATES AND OXALATES.

In case both PO_4''' and C_2O_4'' are present, C_2O_4'' is first removed as described above. This also removes the PO_4''' more or less completely. After dissolving the precipitate in HCl, test a small portion for PO_4'''. If it is still found to be present, conduct the precipitation of the Iron-Zinc group in the manner described under the removal of PO_4''' just above, and then proceed with the detection of the cations, which may be present, in the usual manner.

ANALYSIS OF THE TIN GROUP WHEN GOLD AND PLATINUM MAY BE PRESENT.

(See Noyes and Bray, *Jour. Am. Chem. Soc.*, 29, 178 (1907).)

The Tin group precipitate may consist of As_2S_5, Sb_2S_5, SnS_2, Au_2S_3, PtS_2.

3a. Proceed exactly as in 3a, p. 34.

Residue, As_2S_5, Au_2S_3, PtS_2.	Filtrate, $SbCl_3$, $SnCl_4$.
Add conc. HCl and a few crystals of $KClO_3$, warm, dilute a little, and filter to remove S. If the filtrate is yellow, platinum is probably present.	The separation and identification of antimony and tin are effected in exactly the same manner as on pp. 34–5.

Evaporate until KCl begins to crystallize out, then add water drop by drop until the KCl just dissolves. A yellow precipitate should remain. Cool, filter, and wash with a little saturated KCl solution.

| Precipitate, K_2PtCl_6.	Filtrate, AsO_4''', $Au\ddot{\ddot{u}}$, with KCl.
Dissolve in hot water, and add a few drops of KI solution. A deep red color[1] indicates the presence of platinum.	Add conc. NH_4OH, and then some magnesia mixture. Shake vigorously for some time, filter.

Precipitate, $MgNH_4AsO_4$.	Filtrate, $Au\ddot{\ddot{u}}$, with KCl, etc.
Indicates the presence of arsenic.	Add a small quantity of a saturated solution of oxalic acid, evaporate until the excess of

ammonia is expelled, make just acid with a few drops of the oxalic acid solution, dilute with an equal volume of water, and warm a minute or two on the water-bath. A red precipitate, containing some metallic gold, indicates the presence of gold.

[1] Reduction takes place, the nature of which is not clearly understood.
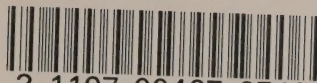
SOLUBILITY TABLE.

Values are for room-temperature, 18°–25°. The *upper number* in each square is the number of grams of anhydrous substance in 100 grams of water, and the *lower number* gram molecules in one liter.

ABBREVIATIONS: s=soluble, rs=readily soluble, vs=very soluble, ss=slightly soluble, es=exceedingly slightly soluble, h=hydrolized in solution, d=decomposes. The order of the metals is that of the electromotive series.

	Cl	Br	I	CN	OH	CO$_3$	S	SO$_4$	C$_2$O$_4$	PO$_4$	AsO$_4$	CrO$_4$	BO$_2$	C$_4$H$_4$O$_6$
K	32.95 / 3.9	65.86 / 4.6	137.5 / 6.0	vs	142.9 / 18.	108.0 / 5.9	vs	11.11 / 0.62	30.3 / 1.6	rs	rs	63.1 / 2.7	vs	vs
Na	35.86 / 5.42	88.76 / 6.9	177.9 / 8.1	vs	116.4 / 21.	19.39 / 1.8	vs	16.83 / 1.15	3.34 / 0.24	9.3 / 0.65	30.0 / 1.4	2.6 / 3.3	2.6 / 0.13	vs
Li	77.79 / 13.3	168.7 / 12.6	161.5 / 8.5	rs	12.04 / 5.0	1.3 / 0.17	vs	35.7 / 2.8	7.22 / 0.69	0.04 / 0.004	ss	111. / 6.5	2.6 / 0.15	s
Ba	rs	vs	vs	rs	3.5 / 0.2	0.002 / 0.0_49	s / h	0.0_325 / 0.0_41	0.009 / 0.0_342	es	0.05 / 0.001	0.0_338 / 0.0_415	ss	0.026 / 0.0_314
Sr	rs	rs	vs	rs / d	0.7 / 0.06	0.001 / 0.0_47	s / h	0.011 / 0.0_362	0.005 / 0.0_328	es	es	0.12 / 0.006	ss	0.112 / 0.0_347
Ca	rs	vs	vs	s / d	0.12 / 0.016	0.0013 / 0.0_313	s / h	0.2 / 0.015	0.0_36 / 0.0_47	ss / h	es	rs	ss	0.016 / 0.0_46
Mg	rs	vs	vs	s	0.0_39 / 0.0_315	ss	h	rs	0.03 / 0.0027	ss	es	rs	ss	0.8 / 0.005
Al	rs	s	s	h	es	h	h	rs	s	es	es	h	h	s
Mn	rs	vs	vs	h	0.0_355 / 0.0_46	es	0.0_363 / 0.0_472	rs	0.05 / 0.0_33	es	es	h	es	ss
Zn	vs	vs	vs	es	0.0_313 / 0.0_413	0.001 / 0.0_41	0.0_369 / 0.0_471	rs	0.008 / 0.0_45	es	es	h	h	ss
Cr	s	vs		h	es	h	h	rs	es	ss	ss	ss	es	s
Cd	vs	rs	rs	1.7 / 0.12	0.0_326 / 0.0_418	es	0.0_313 / 0.0_59	rs	0.008 / 0.0_44	es	es	es	ss	s
Fe (ous)	rs	vs	vs		0.0_37 / 0.0_48	es	0.0_362 / 0.0_470	rs	0.02 / 0.0_314	es	es	es	h	0.9 / 0.004
Fe (ic)	rs	vs			es	h	d	rs	rs	h	es	h	es	s
Co	rs	s	vs	ss	es	es / h	0.0_338 / 0.0_442	rs	es	es	es	es	ss	ss
Ni	rs	vs	vs	ss	es	es / h	0.0_336 / 0.0_440	rs	ss	es	es	h	es	ss
Pb	1.0 / 0.035	0.83 / 0.023	0.06 / 0.0013	es	0.0017 / 0.0_47	0.0_56 / 0.0_62	0.0_49 / 0.0_536	0.0042 / 0.0_314	0.0_318 / 0.0_66	0.0_413 / 0.0_616	es	0.0_42 / 0.0_65	es	es
Cu	rs	s		es / d	es	es	0.0_433 / 0.0_535	rs	es	es	es	es	es	0.02 / 0.0_31
Bi	h	h	es	es	es	es	0.0_418 / 0.0_635	h	es	es	es	oxy 0.0_48 / 0.0_51	es	es
Hg (ous)	0.0_447 / 0.0_520	0.0_54 / 0.0_614	0.0_72 / 0.0_96	h	oxide es	h	d	0.06 / 0.0012	es	h	es	es	h	es
Hg (ic)	s	0.6 / 0.017	0.005 / 0.0_31	rs	0.005 / 0.0_324	h	0.0_512 / 0.0_75	h	es	es	ss	h	h	s
Ag	0.0_315 / 0.0_411	0.0_58 / 0.0_64	0.0_62 / 0.0_71	0.0_42 / 0.0_516	0.002 / 0.0_52	0.0017 / 0.0_46	0.0_412 / 0.0_65	0.8 / 0.025	0.0037 / 0.0_312	0.0_364 / 0.0_415	es	0.0025 / 0.0_475	ss	0.2 / 0.0_38

Additional data: SnS$_2$, 0.0_42 / 0.0_51, Sb$_2$S$_3$, 0.0_317 / 0.0_55, As$_2$S$_3$, 0.0_45 / 0.0_52, MgNH$_4$PO$_4$.6H$_2$O, 0.011 / 0.0_34